PB85-116853

Methods/Materials Matrix of Ultimate Disposal Techniques for Spilled Hazardous Materials

Battelle Pacific Northwest Labs., Richland, WA

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

Oct 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-116853

EPA-600/2-84-170
October 1984

METHODS/MATERIALS MATRIX OF ULTIMATE DISPOSAL TECHNIQUES FOR SPILLED HAZARDOUS MATERIALS

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SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-84-170	2.	3. RECIPIENT'S ACCESSION NO. PB85 116853
4. TITLE AND SUBTITLE METHODS/MATERIALS MATRIX FOR ULTIMATE DISPOSAL TECHNIQUES FOR SPILLED HAZARDOUS MATERIALS		5. REPORT DATE October 1984
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) B.W. Mercer, G.W. Dawson, J.A. McNeese, and E.G. Baker		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Pacific Northwest Laboratories Battelle Memorial Institute Richland, Washington 99352		10. PROGRAM ELEMENT NO. CBRD1A
		11. CONTRACT/GRANT NO. 68-03-2494
12. SPONSORING AGENCY NAME AND ADDRESS Municipal Environmental Research Laboratory - Cin, OH Office of Research & Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED Final 2/15/77-7/7/80
		14. SPONSORING AGENCY CODE EPA 600/14

15. SUPPLEMENTARY NOTES

Project Officer: John E. Brugger, (201) 321-6634

16. ABSTRACT

A study was undertaken to evaluate conventional and novel methods for the ultimate disposal of spilled or released hazardous substances. Disposal methods studied include incineration, pyrolysis, landfilling, fixation, biological treatment, and chemical treatment. Applications of and problems associated with each of these disposal methods are discussed. Special emphasis is given to spills of highly toxic and persistent hazardous materials.

An annotated matrix was prepared to provide a full assessment of conventional disposal options for each class of hazardous material and for mixtures thereof. The hazardous materials are grouped according to physical/chemical properties and placed in juxtaposition with the form (liquid, sludge) or composition of the spill residue containing the hazardous material (e.g., mixtures with water, grass, sand, debris, etc.). The disposal options are priority-ranked for each given set of conditions. The annotation describes each disposal option and evaluates the influence of spill-situation parameters on the disposal method with regard to effectiveness, cost, safety, availability of equipment and materials, and short and long-term hazards.

Deficiencies in conventional disposal methods, such as secured landfills, are identified. An amended matrix, which supplements the matrix based solely on conventional methods, includes novel disposal methods that show strong potential for filling some of the gaps in existing disposal technology.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 129
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

DISCLAIMER

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CAUTIONARY NOTE TO READER

This study was conducted during the late 1970's and contains dated information pertaining to U.S. Environmental Protection Agency regulations and policies. Consequently, the reader is reminded to retain the same perspective that would be appropriate in reading any document several years after its initial preparation. Particular care should be exercised when considering the cost data and references to "current and anticipated" regulations and Agency policies, many of which have now become much more demanding. It was decided to publish this report, even though portions are out of date, based on the potential benefits that could be derived from the technical content of the study.

FOREWORD

The U. S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This study was undertaken to evaluate conventional and novel methods for ultimate disposal of spilled hazardous materials. Disposal methods studied include incineration, pyrolysis, landfilling, fixation, biological treatment, and chemical treatment. Applications of these disposal methods to spilled hazardous material residues is discussed with special emphasis given to spills and releases of highly toxic and persistent hazardous substances. The problems related to disposal of mixtures of hazardous materials with other substances such as processing sludges, soil, debris, and various aqueous inorganic and organic dilutents is also discussed. The report contains information that can be used by on-scene coordinators, as well as by waste generators and haulers, the hazardous waste disposal industry, and environmentalists who seek a better understanding of waste disposal options.

Francis T. Mayo, Director
Municipal Environmental Research Laboratory

ABSTRACT

Conventional and novel methods for the ultimate disposal of spilled or released hazardous substances are evaluated. Disposal methods reviewed include incineration, pyrolysis, landfilling, fixation, biological treatment, and chemical treatment. Applications of these disposal methods to hazardous material residues is discussed with special emphasis given to spills or releases of highly toxic and persistent hazardous materials. The problems related to disposal of mixtures of hazardous materials with other substances such as processing sludges, soil, debris, and various aqueous and organic dilutents is also discussed.

An annotated matrix was prepared to provide a full assessment of conventional disposal options for each class of hazardous material and for mixtures thereof. The hazardous substances are grouped according to physical/chemical properties and put in juxtaposition with the form of the spill or release residue containing the hazardous material (e.g., mixtures with water, grass, sand, debris, etc.). The disposal options are priority-ranked for each given set of conditions. The annotation describes each disposal option and evaluates the influence of spill-situation parameters on the disposal method with regard to effectiveness, cost, safety, availability of equipment and materials, and short-and long-term hazards. Deficiencies in conventional disposal methods are identified. An amended matrix which supplements the matrix based on conventional methods includes novel disposal methods that show strong potential for filling some of the gaps in existing disposal technology.

Maximal use of hazardous waste management facilities located throughout the United States is recommended for disposal of spill and release residuals. These facilities, including secured landfills, will soon be operating under the stringent regulations mandated by the Resource Conservation and Recovery Act, and will therefore provide greater assurance of adequate containment or disposal of hazardous wastes.

This report was submitted in fulfillment of Contract No. 68-03-2494 by Battelle Pacific Northwest Laboratories under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period from February 1977 to July 1980, and work was completed as of September 1982.

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ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support and advice provided by Dr. John E. Brugger of the Municipal Environmental Research Laboratory, Oil and Hazardous Materials Spills Branch, Edison, New Jersey. The authors also wish to thank the following Battelle personnel who participated in the tasks of typing and proofreading of the manuscript: Barbara Roberts, Mary Heid, Darla Kennedy, Marianna Cross, and Nancy Painter. Dr. H. Skovronek, consultant to IT Corporation, prepared the separately issued Project Summary Report. Mr. Gregory N. Bailey, MERL-OHMS Branch, Ms. Darlene Williams and Ms. Joanne Cuoghi, IT Corporation, proofread and retyped the Project Summary Report and the final manuscript.

SECTION 1

INTRODUCTION

With promulgation of the regulations on Hazardous Substance Spills (Section 311 of PL 92-500 the Clean Water Act, as amended), increased effort will be directed to the cleanup and collection of spilled and released materials and the volume of contaminated spill residuals requiring disposal will commeasurately increase. At the same time, regulations mandated by the Resource Conservation and Recovery Act (PL 94-580) will dictate the manner in which that disposal may be conducted. Consequently, much more scrutiny will be placed on spill residual management.

Cleanup activities following spills or releases of hazardous materials or wastes frequently involve the disposal of extraneous matter such as soil, sediment, water, and debris that has become contaminated by the hazardous substance. Disposal methods normally used for the hazardous material alone may no longer be fully applicable in these cases. For example, the recommended disposal method for PCB's is incineration at 1200°C with 3% excess oxygen and a dwell time of 2 seconds or at 1600° C with 2% excess oxygen and a dwell time of 1.5 seconds.(1) Under these conditions destruction of PCB's in a relatively pure form or diluted with an appropriate solvent is a practical, proven disposal method, whereas destruction by incineration of small amounts of PCB's intermixed with large quantities of sediments is not as practical. An alternate disposal method that is consistent with good environmental protection practices must be selected for this mixture.

The preceding example addresses a single substance and a single technology. Disposal of spill residuals from over 650 designated hazardous materials(2-4) can involve a wide variety of pretreatment and disposal methods ranging from a simple water flush to complex chemical treatment followed by burial of any residuals in a secure landfill. Further, spills and releases need not consist of a single pure substance. In addition to the 650 designated hazardous substances spills may involve numerous mixtures containing these substances in the form of industrial process streams and liquid and solid wastes (RCRA wastes). Spillage of either discrete hazardous materials or process streams and wastes containing these materials can create a waste form with properties that are substantially different than those of the original material. Chromium sulfate solution spilled on soil, for example, becomes much less of a threat to aquatic life than the original solution spilled in a stream because the soil ties up the chromium ion, thereby reducing its availability by leaching to aquatic life forms. Indeed, the chromium may be so diluted and so tightly held by the soil that the soil mixture would not qualify as a hazardous waste and could safely be disposed in a sanitary landfill instead of in a secure landfill as would be the case for nearly pure chromium sulfate.

Heretofore, mixtures of hazardous materials with extraneous matter have been largely dealt with on a judgmental basis since no uniform criteria were available to classify mixtures. Hence, considerations such as those discussed above were performed on an ad hoc basis. However, EPA's Office of Solid Waste is currently developing criteria for designating hazardous wastes that should simplify the problem of classifying mixtures of hazardous material with inert matter. Clean-up debris from spills of designated hazardous materials will be defined generically as hazardous wastes. For other spill residuals, a significant element of these criteria will be a leach test to determine the availability or mobility of hazardous substances in the mixture (EP-toxicity test, 40 CFR 261.24). Consequently, spills of hazardous material have the potential of creating a hazardous waste which, under impending regulations, must be disposed of by an authorized method. In the case of small spills of hazardous materials not specifically cited in the RCRA regulations, tests (ignitibility, corrosivity, EP-toxicity, reactivity) to classify spill residual mixtures may not be economically justified if--for example--the cost of burial in a secure landfill is less than the combined costs of the tests and burial in an ordinary sanitary landfill. For spills involving large quantities of spill residual mixtures, conducting the tests could save substantial disposal costs.

The following discussion is directed to a description of the capability of current technology to cope with spill residuals management. Special emphasis is placed on identifying gaps in that technology and on specifying alternatives that may fill these gaps.

SECTION 2

SUMMARY AND CONCLUSIONS

Conventional technology is considered satisfactory for the ultimate disposal of the majority of waste residuals resulting from hazardous spills and releases. Hazardous materials exhibiting low toxicity and persistance generally do not represent a disposal problem; however, continued effort is needed to assure use of the proper method in each spill situation. Maximal use of hazardous waste management facilities located throughout the nation is recommended for disposal of spill residuals. These facilities are more likely to have the special equipment and staff expertise needed to dispose of the residuals than are sewage treatment or industrial waste treatment plants. Furthermore, the hazardous waste disposal industry will soon be operating with permits granted through regulations mandated by the Resource Conservation and Recovery Act. As such, selection of a firm that has been granted a permit carries some degree of assurance the proper disposal practices will be employed. The need for effective disposal has now been enhanced significantly by the passage of CERCLA ("Superfund") legislation (P.L. 96-510.)

Areas where conventional technology is considered inadequate include the disposal of highly toxic and persistent spill residuals intermixed with extraneous matter including soil, sediments and debris. Incinerators, for example, are generally not practical for economically decomposing organic substances intermixed with substantial quantities of noncombustible material such as soil. An effective leaching technique is a potential alternative for recovering the residual for disposal. Currently, research is planned to evaluate the effectiveness of leaching (or solvent extraction) over a range of different materials and conditions.

The EPA's Oil and Hazardous Materials Spills Branch in Edison, New Jersey, is currently sponsoring several research programs to develop alternate methods of decomposing and detoxifying hazardous organic substances such as persistent chlorinated hydrocarbon pesticides. The methods under investigation include: 1) degradation by liquid alkali metals, 2) biological degradation with specially adapted microbial cultures, and 3) decomposition through oxidation by bromine (with recovery of Br_2 from HBr). These methods are aimed at the disposal of small quantities of highly toxic material which may or may not be mixed with large quantities of extraneous matter.

The lack of suitable incinerators and public objection to their siting in many areas of the country are other problems associated with the destruction of hazardous organics. In addition to the chemical and biological techniques identified above, incineration in cement kilns and microwave or plasma arc decomposition show potential for destruction of highly toxic organics.

The disposal of highly toxic heavy metals such as cadmium and arsenic pose a special problem since these substances cannot be decomposed as in the case of organic materials where the toxicity is dependent on structure rather than on elemental composition. One potential alternative is incorporation of these metals in a matrix such as glass that has a very low leaching rate. Fixations of heavy metals can effectively minimize the mobility of toxic heavy metals when a sufficiently low leach rate can be maintained over an indefinite (but long) time period. Fixation in glass, although higher in cost than other chemical waste fixation methods, is a leaching candidate for achieving long-term stability with low leach rates. Fixation in other matrixes (e.g. asphalt, plastics, cement-like compositions, synthetic rocks) are other alternatives.

SECTION 3

RECOMMENDATIONS

The continued development and demonstration of novel disposal methods are recommended to overcome current deficiencies in conventional technology and the lack of adequate disposal facilities in sufficiently remote and controlled access areas. This effort should focus on methods that achieve near-total destruction of hazardous organic materials and permanent containment of highly toxic metals. Landfill disposal of highly toxic persistent hazardous materials should be phased out as the primary containment method for these materials since the long-term integrity of most landfills cannot be assured (or "insured", as may be required under "Superfund" regulations).

Incineration is the standard technique for destruction of hazardous organic materials. However, facilities properly designed to accomplish this task are not widely available. Current efforts to demonstrate the use of cement kilns, smelters, blast furnaces, and other large processing units for destruction of these wastes should be intensified. Since cement kilns, for example, cannot accept all waste forms, some attention should be directed to development of mobile facilities to modify residuals to acceptable forms, thus extending the applicability of kilns. In addition, alternate methods for chemical destruction should be demonstrated to provide coverage in areas where incinerator facilities are not available. These alternate chemical disposal units should be equipped to destroy the highly-toxic persistent spill residuals that are usually transported in small shipping containers, such as drums, as opposed to bulk shipping in tank cars. The disposal units may, therefore, be relatively small in size to allow transport to the spill site or they may be constructed from locally available equipment and materials. These units should also be equipped to handle debris that is intermixed with the spill or release residual. Studies are currently being conducted under EPA sponsorship to evaluate oxidation by bromination, reduction with elemental sodium, and biochemical degradation with specific cultures to dispose of hazardous organic spill residuals. Methods of leaching spill residues from debris are also being developed under EPA sponsorship and rapid implementation of these methods will greatly aid in recovery and disposal efforts.

Much more work is needed to demonstrate adequate fixation methods for the highly toxic metals. Fixation should be sufficiently "tight" to ensure that the leach rate is low enough to avoid the presence of toxic levels of these metals in the leachate. Furthermore, the fixed waste should exhibit essentially permanent stability under anticipated environmental conditions (e.g., weathering, leaching, land use). Fixation in glass is presently being investigated as a potential method for containment of toxic heavy metals (many radionuclides have been successfully bound in glassy matrixes).

The need to upgrade and actively involve the hazardous waste management industry for disposal of hazardous spill residuals should be emphasized by EPA and state representatives who are responsible for cleanup activities following a spill. An up-to-date listing of hazardous waste disposal facilities in each region should be maintained and made available to personnel responding to spills of hazardous materials. Further, efforts should be made to ensure that response personnel are familiar with emerging hazardous waste regulations since these will prescribe legal constraints on the management of spill residuals.

SECTION 4

REVIEW OF REPORTED SPILLS

Information concerning recent spills and releases of hazardous materials in the United States was reviewed to determine the current frequency of these events, the countermeasures taken, the types of problems encountered, and the disposal methods used for spill residuals.

SPILL OCCURRENCES

Types of Material

Substances designated as hazardous materials (for the purposes of this project) are listed in alphabetical order in Appendix A. This list was compiled from the Environmental Protection Agency's list of Hazardous Substances,(2) the U.S. Coast Guard's CHRIS Hazardous Chemical Data(3) and pesticide data.(4) In addition to the materials included in Appendix A, mixtures of these same materials and wastes designated as hazardous under RCRA regulations(5) are also considered to be hazardous materials. Industrial wastes consisting of sludges, off-spec materials, residues, bottoms, etc. which contain varying concentrations of hazardous substances are typical examples of mixtures from manufacturing and processing operations. Debris that becomes contaminated with spilled hazardous material is another type of mixture that may be a hazardous waste. Consultation with private firms whose business is cleaning up hazardous material spills reveal that contaminated soil or sediments were the most frequently encountered contaminated debris.

Frequency of Spillage

Approximately 13,000 spills of oil and hazardous materials occur in waterways of the United States each year.(6) Over 60% of the reported spills involve oil substances for which mandatory reporting requirements have been in effect since 1970. It has been estimated that 3000 spills of hazardous materials excluding oil enter the nation's navigable waters each year.(8) Land spills that do not directly threaten water are not covered under PL 92-500 (Clean Water Act) but may be covered under RCRA, CERCLA ("Superfund") or the Clean Air Act.

DISPOSAL OF SPILL RESIDUALS

Methods Used

A survey of waste disposal firms disclosed that landfilling is the most common method used for disposing of oil spill residuals that cannot be recovered for re-use. A review of 78 randomly selected, hazardous material spill reports received by the Oil and Hazardous Materials Spill Branch of the EPA's Municipal Environmental Research Laboratory at Edison, New Jersey, during the period December 1975 to May 1977 reveals that no action for spill cleanup occurs in 36% of the spill events. This is followed by the use of a water wash in 24% of the events as shown in Table 1.

TABLE 1. Disposal Methods Employed for Hazardous Spill Residuals

Method Used	No. of Incidents	% of Total
None	28	36
Water Wash	19	24
Chemical Treatment	9	11
Recovery	6	8
Landfill	2	3
Biological Treatment	1	1
Nothing Reported	13	17
Total	78	100

Most of the hazardous material spills other than oil involve the widely used chemicals of industry and agriculture such as ammonia and sulfuric acid. A water wash is frequently used for these materials when the spill occurs on land. No action whatsoever is usually taken for small spills of anhydrous ammonia since this material quickly evaporates to the air. Of particular concern are the spills of highly toxic materials such as certain pesticides. One of the most widely publicized pesticide spills occurred when a plant in Virginia, producing Kepone, a chlorinated hydrocarbon, allowed spills and off-standard batches of this material to be discharged to the local sewage treatment plant and then to the James River.(9) A considerable quantity of river sediments and soil has become contaminated with Kepone as a result. The cleanup and disposal problems associated with this Kepone spill are enormous. Two small spills of pesticides occurred on highways, one involving 60 liters of a 1% solution of a chlorinated hydrocarbon and another involving 210 liters of an organophosphate compound. No cleanup action was taken in the former while sand was used to sorb the latter. (The contaminated sand was disposed in a landfill.)

A large number of spills and releases of pesticides or other extremely toxic materials occur but are not reported. Because of the small number actually reported, it is difficult to assess the adequacy of the disposal methods used. However, it is judged that landfill disposal, frequently as surreptitious dumping, is most commonly used for these materials and may rank only slightly ahead of illegal disposal in sewers or watercourses.

Disposal Problems Encountered

Review of the literature and consultation with private firms reliably dealing with hazardous materials spills indicate that the most frequent problem encountered is locating a disposal site for the spill residual. Following the publicity usually associated with a spill, local residents generally do not favor the disposal of spill residuals in nearby landfills even though the landfill may be suitable to receive this waste. Furthermore, some states have become quite restrictive in allowing hazardous wastes to be shipped in from other states for disposal and court tests are expected.

Improper design, location, and operation of landfills are well-known problems that can result in loss of confinement of the hazardous materials disposed at these sites. The Environmental Protection Agency has proposed regulations for disposal of hazardous wastes.(5) When promulgated and ultimately amended as necessary, these regulations will dictate the reporting, packaging and labeling methods that must be employed for any waste defined as hazardous. As a result, many of the options now open for spill residuals management will be legally closed.

Poor communication between regulatory agencies and disputes between these agencies concerning jurisdiction over the spill incident have been reported as frequently occurring problems by private contractors involved in the business of cleaning up spills. The problems are viewed as transient and remediable as areas of jurisdiction are defined and regulations promulgated.

SECTION 5

DESCRIPTION AND ASSESSMENT OF CONVENTIONAL DISPOSAL ALTERNATIVES

In the following sections, techniques leading to ultimate disposal of hazardous or toxic materials are reviewed. Many of these methods are not ultimate disposal techniques in themselves but do constitute unique and necessary steps in an ultimate disposal process. For this reason these processes such as low-temperature fixation and certain types of precipitation, are included in discussions of ultimate disposal techniques. However, steps that have very general application, such as sedimentation and filtration, are considered as disposal pre-treatment procedures.

BIOLOGICAL TREATMENT

General Description

Biological treatment processes are those which utilize microorganisms (mainly bacteria) to oxidize dissolved and colloidal organic matter in wastewaters. (Anaerobic treatment is not being considered here.) The microorganisms metabolize the organic matter in wastewater to yield energy for synthesis, reproduction, motility, and respiration. Biological utilization of organic compounds involves a series of enzyme-catalyzed reactions. Simple dissolved or soluble organic compounds are readily transported through the cell walls of microorganisms and oxidized (or accumulated). When some microbial cells come into contact with complex organics, extra-cellular enzymes are released by the cells to hydrolyze such high molecular weight materials as proteins, sugars, and fats into diffusible fractions, enabling their transport though the cell wall for assimilation. The larger, more complex organic compounds are thus metabolized at a much slower rate. Some complex organic compounds are not or cannot be degraded by biological oxidation; these are called "refractory" organic compounds. Other compounds can be metabolized by the microorganisms at low concentrations but are toxic at high concentrations. In the case of toxic substances, a period of acclimation is frequently necessary to allow the microorganisms to "adjust" to these materials. A different population of microorganisms (including mutants) may develop during the acclimation period and subsequently provide more effective treatment.

The relationships between metabolism, energy, and synthesis are important in understanding biological treatment systems. The primary product of metabolism is energy, and the chief use of this energy (usually in the form of "high energy" organic phosphates) is for synthesis. Energy release and synthesis are coupled biochemical processes, where the maximum rate of synthesis occurs simultaneously with the maximum rate of energy yield (maximum rate of metabolism). This process may be simplistically represented by the following reaction:

soluble organics + O_2 + microorganisms $\rightarrow$ CO_2 + H_2O + energy + microorganisms.

(Nitrogen and phosphorus compounds, trace elements, and other "requirements" must be available.) The primary purpose of most biological treatment processes is to convert soluble or colloidal organic substrates to CO_2, H_2O, and settleable matter (usually biomass or sludge) that can be removed by sedimentation. In the case of hazardous or toxic substances, note that complete removal may not be achieved and that the metabolites from the process may also be toxic in themselves. Dilution (or other pre-treatment) may be necessary if biochemical conversion is to achieve the desired reductions in the quantity of the pollutants being biodegraded. (For optimized performance, the microorganisms (bacteria, fungi, algae, protozoa) almost unilaterally set "workplace" conditions: oxygen, pollutant, food, salinity, nutrient, illumination, and population levels, pH, temperature, etc.)

Efficient and successful biological oxidation of organic wastes requires a minimal quantity of nitrogen and phosphorus for the synthesis of new cells. In addition, trace or larger quantities of several other elements such as sodium, potassium, calcium, magnesium, iron, manganese, vanadium, copper, nickel, etc. are required. The "trace" elements are usually present in natural waters in sufficient quantities to satisfy requirements for microbial metabolism. However, nitrogen and phosphorus levels are sometimes deficient in wastewater substrates and cause reductions in removal efficiencies of biological treatment systems. In such cases, nutrients must be added to supplement those in the wastewater substrate. Nitrogen should be added as a supplement in the form of ammoniacal nitrogen, because nitrite and nitrate nitrogen are not so readily available for microbial usage. Several soluble phosphorus salts that are readily assimilated by microorganisms are available. Generally, a BOD:N:P ratio of 100:5:1 is thought to be the optimum ratio of nutritional requirements for microorganisms utilized in biological waste treatment. (BOD or biochemical oxygen demand is the term applied to signify the strength of biodegradable organics in wastewater and is defined generally as the amount of oxygen required by microorganisms to biologically oxidize a given quantity of organics. The more concentrated the organic waste material, the higher the BOD. Some workers prefer measurement of COD (carbon oxygen demand) or TOC (total organic carbon).

Biologically degradable organics in wastewater can be dissolved in solution or be in solid form. Only dissolved (or soluble) organics can be metabolized within microbial cells. In wastewaters, the undissolved forms of biodegradable organics may be colloidal or suspended solids. These may be hydrolyzed to soluble forms by exoenzymes released from within microbial cells. (These remarks apply chiefly to bacterial action.)

There are a number of approaches that utilize biological processes. These include activated sludge units, biological filter systems, aerated lagoons, oxidation ponds, land application systems and anaerobic fermentation reactors. Selection of a particular system is generally based on wastewater characteristics and volume, desired levels of pollutant removal, and location. Biological systems generally achieve 50 to 90% BOD removal although higher removal can be attained under optimum conditions. Activated sludge units, biological filters, and stabilization ponds are the most widely used biological treatment processes. These processes along with land application--a widely used industrial process--are discussed below.

Activated Sludge Process

The activated sludge process involves the production of a suspended mass of microorganisms in a reactor to biologically convert soluble organic compounds in wastewater to carbon dioxide, water, additional microorganisms, and energy. In operation of the activated sludge process, wastewater containing soluble or finely suspended organic compounds is fed to the aerobic reactor (aeration tank) which furnishes 1) air required by microorganisms to biochemically oxidize the waste organics, and 2) mixing to insure intimate contact of microorganisms with the organic waste (see Figure 1). The aerobic reactor contents are referred to as mixed liquor suspended solids (MLSS). In the vigorously mixed aerobic reactor, the organic wastes are metabolized to provide energy and growth factors for the production of more microorganisms with the release of carbon dioxide and water as metabolic end products. The organic waste compounds may thus be degraded to innocuous end products (including inorganic salts) and also utilized to form more microorganisms. The MLSS flows from the aeration tank to a sedimentation tank, which provides quiescent settling to allow separation of the biological solids from the treated wastewater. The treated and clarified water is collected and discharged as process effluent. Most of the settled biological solids are recycled (as return activated sludge) to the aerobic reactor to provide an activated mass of microorganisms for continuous treatment of incoming wastewater. Some of the settled biological solids are wasted to maintain a proper balance in the population of microorganisms in the MLSS of the aerobic reactor.

The activated sludge process is very flexible and can be utilized for the treatment of almost any type of biodegradable waste. The original process configuration is called the conventional activated sludge process, and has been modified in numerous ways. In the original conventional (or plug flow) activated sludge process, wastewater and return activated sludge enter one end of a long narrow aeration tank and are mixed in a longitudinal direction as flow occurs along the length of the tank. The long, rectangular aeration tanks are generally designed so that the total tank length is 5 to 50 times the width. Air is supplied by bubble type diffusers that cause a spiral and helical flow of the mixed liquor as it flows to the exit end of the tank. The spiralling flow along the length of the tank is a uniform, straight-line flow pattern, hence the name "plugflow." Conventional and other activated sludge process variations are discussed in References 10-15.

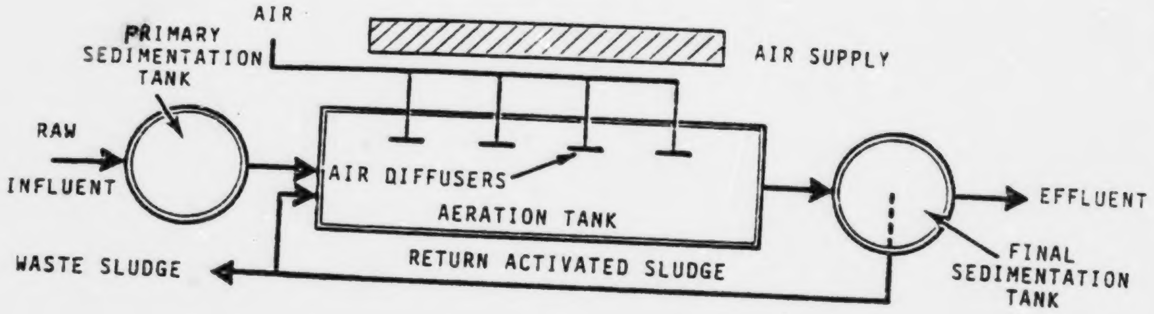

AIR
PRIMARY SEDIMENTATION TANK
AIR SUPPLY
RAW INFLUENT
AIR DIFFUSERS
AERATION TANK
EFFLUENT
WASTE SLUDGE
RETURN ACTIVATED SLUDGE
FINAL SEDIMENTATION TANK

FIGURE 1. Activated Sludge Process

A process that differs significantly from plug flow is the complete mix activated sludge system which has become one of the more popular designs in recent years because of its greater ability to withstand shock loads and the introduction of new, chemically different toxic substances. In the complete mix system, influent waste water is uniformly mixed throughout the entire aeration basin as rapidly as possible. The mixing tends to produce a uniform organic load through the entire contents of the aeration basin. Since the influent wastes are mixed throughout the aeration basin, the entire basin volume acts to buffer hydraulic surges and organic shock loads. For example, it has been shown that 100 mg/l of phenol is toxic to the conventional activated sludge process, whereas a loading of 2000 to 3000 mg/l phenol was not toxic in the complete mix system.(16) This feature enables the establishment of near-equilibrium conditions for stable operation.

Trickling Filter

The trickling filter process consists of a fixed bed of coarse, rough material over which wastewater is intermittently or continuously distributed in a uniform manner by a flow distributor (see Figure 2). Microorganisms grow on the surface of the filter media forming a biological or zoogleal slime layer. As wastewater flows downward through the filter, the fluid passes over the layer of microorganisms. Dissolved organic material and nutrients in the wastewater are taken up by the zoogleal film layer for utilization by the microbial population. Oxidized end products are released to the liquid and collected in the underdrain system for discharge via the effluent channel. Aerobic conditions are maintained by natural draft, wind forces, temperature differences (filter vs. ambient), and entrainment of air by the wastewater as this fluid passes through the filter bed. A trickling filter will operate properly so long as the void spaces are not clogged by solids or by excessive growth of the zoogleal film layer. The zoogleal film layer grows and gradually increases in thickness to the point that the hydraulic shear force from the downward flow of wastewater causes portions of the film layer to slough off the filter media. The sloughed filter film is separated as sludge in secondary clarification units.

The trickling filter process has some advantage in reliability over the activated sludge process. The reservoir of captive microorganisms that are readily adjustable to shock loadings is the basis of its dependability. The trickling filter achieves consistent BOD removals in the face of fluctuating hydraulic and organic demands. The recent introduction of plastic media (instead of minerals, slag, etc.) has resulted in shortened detention time requirements through the filter, though BOD removal is still limited to a maximum of about 85%. A second innovation recently introduced is the recirculation of biofloc from the system back through the filter, achieving high BOD/COD removal efficiency (COD = carbon oxygen demand). The recirculated trickling filter is similar to an activated sludge process, and attains the same high (90%) BOD removal. Additional information concerning the design and operation of trickling filters is available in References 12, 17, 18 and 19.

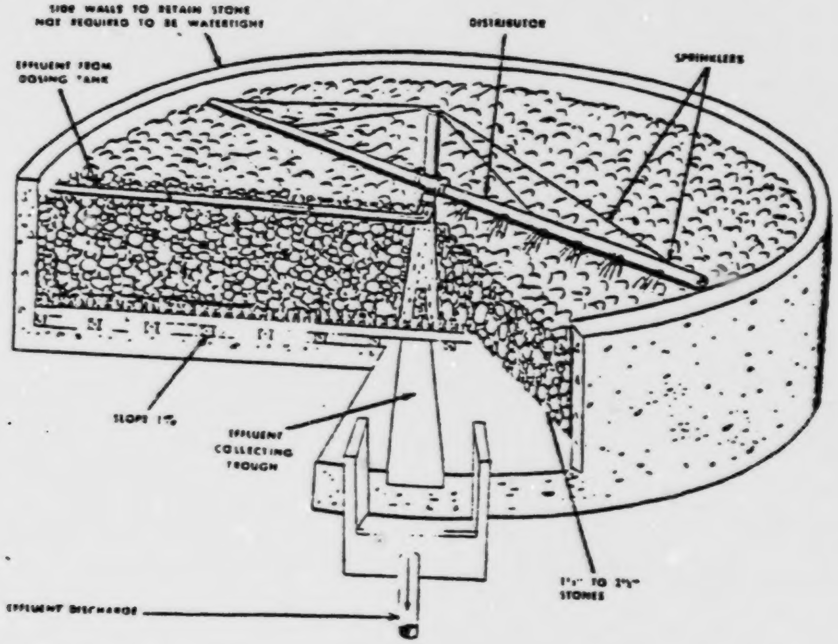

SIDE WALLS TO RETAIN STONE
NOT REQUIRED TO BE WATERTIGHT
DISTRIBUTOR
SPRINKLERS
EFFLUENT FROM
DOSING TANK
SLOPE 1%
EFFLUENT
COLLECTING
TROUGH
1½" TO 2½"
STONES
EFFLUENT DISCHARGE

FIGURE 2. Trickling Filter Diagram

Waste Treatment Lagoons

Wastewaters may be effectively stabilized by the natural biological processes that occur in relatively shallow ponds. Stabilization is attained by photosynthesis by algae and/or oxidation by bacteria. Waste stabilization ponds (or lagoons, as they are sometimes called) are very popular with small communities because of their low construction and operating costs, which offer a significant financial advantage over other recognized treatment methods.

Waste stabilization ponds are generally classified according to the nature of the biological activity and environment within the pond. Thus stabilization ponds are classified as aerobic, aerobic-anaerobic (or faculative), and anaerobic. A waste stabilization pond system may include a single pond or a number of ponds in series or parallel. Also, different classifications of ponds may be utilized in series, i.e., aerobic followed by an anaerobic or vice versa. This switch between aerobic and anaerobic conditions is usually done to effect greater treatment efficiencies than can be achieved via a single pond type.

Aerobic ponds are additionally separated into two categories based on whether natural or artificial methods are utilized to supply oxygen to the bacteria in the pond. In natural aeration, oxygen is supplied by surface aeration and by algal photosynthesis: such ponds are generally termed "oxidation ponds." Mechanical aeration units can be used to artificially supply oxygen to the bacteria. The artificial (mechanical) aeration process is essentially the same as the activated sludge process, but occurs without recycle of microorganisms. Mechanically aerated ponds are generally termed "aerated lagoons."

Oxidation ponds utilize algae and bacteria in a symbiotic relationship to stabilize waste organics. The oxygen released by the algae through the process of photosynthesis is utilized by bacteria for the aerobic degradation of organic matter. The nutrients and the carbon dioxide released via bacterial respiration are, in turn, used by the algae. During the daylight hours, increased algal photosynthetic activity occurs and oxygen concentrations may reach supersaturation levels. Generally, solids will accumulate and settle in an oxidation pond because of the lack of mixing. The accumulated settled solids form an anaerobic sludge layer on the bottom, and the pond becomes an aerobic-anaerobic (faculative) pond. Oxidation ponds generally are relatively shallow (3 to 5 ft deep). (20) (1 ft = 0.3m)

Aerated lagoons are an outgrowth of the development of the completely mixed activated sludge process. Surface mechanical aerators are applied to overloaded oxidation ponds. Aerated lagoons are generally constructed at depths of 8 to 15 ft.(20,21) Generally, no consideration is given to algae for supplying dissolved oxygen because the pond surface is turbulent and the growth of algae is inhibited.

Aerobic-anaerobic (facultative) ponds were historically known as stabilization ponds. The symbiotic algae-bacteria relationship is utilized to its fullest in these ponds. The ponds are generally 3 to 8 ft in depth. The solids settle to the bottom and eventually decompose anaerobically. The decomposition results in the interchange of anaerobic decomposition byproducts with aerobic oxidation byproducts between the upper and lower portions of the pond.

Anaerobic ponds were the inevitable result of the widespread use of "stabilization" ponds (faculative) where the organic loading rates became excessive and caused anaerobic conditions throughout the pond. The symbiotic stabilization relationship failed but was replaced by an anaerobic stabilization process where waste organics are stabilized by anaerobic, methane-forming bacteria similar to those which ocur in anaerobic digesters.

Land Application

Land application as a treatment and disposal method utilizes the interactions between plants and the soil surface to effectively stabilize many different types of wastes. The combination of plants and soil can serve as a natural biological filter(22,23) since most top soils already contain the microorganisms needed for biochemical decomposition of organic matter. In addition, physical and chemical processes can occur within the soil to neutralize either strong acids or bases, remove inorganic constituents and filter out suspended solids. Passage of the Federal Water Pollution Act PL 92-500 has focused attention on land application as an alternative for effective treatment and disposal of wastewaters and sludges to comply with zero discharge requirements slated for 1985.

General criteria for judging the suitability of land disposal for a particular waste follow:(24)

1. The organic material must be biologically degradable at reasonable rates.
2. The waste must not contain materials in concentrations toxic to soil microorganisms. Since some toxic materials may accumulate through adsorption or ion exchange and approach toxic levels after prolonged operation, there must be reasonable assurance that this effect can either be prevented or mitigated.
3. The organic waste must not contain substances that will adversely affect the quality of the underlying groundwater. In many instances, decisions relative to this aspect of land disposal systems are difficult to make because of the uncertain nature of available estimating techniques. Nitrate-or nitrate-forming compounds are often a limiting factor (nitrification) in this regard.
4. The waste must not contain substances that cause deleterious changes to the soil structure, especially its infiltration, percolation, and aeration characteristics. An imbalance of sodium is the most common problem of this kind.

Land application is suitable for disposal of many different hazardous materials including oil residues.(25)

Application of liquid wastes to land is generally accomplished by irrigation methods. Solids may be applied through the use of mechanical spreading devices installed on the truck or carrier used to haul the waste to the disposal site.

Assessment of Biological Methods

Biological degradation is probably the most common method of ultimate disposal for organic and organic-contaminated hazardous materials spill residuals. The use of this method is perhaps not intentional in most cases but it occurs, nevertheless, as a natural phenomena either in the soil or the water that receives biodegradable organic hazardous material spill residuals. Over half of the hazardous materials listed in Appendix A are capable of biodegradation although, in many instances, dilution or some form of pretreatment (e.g., neutralization) is needed to allow the process to occur.

Intentional use of biological degradation processes, as in a municipal sewage treatment plant, is a viable option for disposal of biodegradable hazardous materials spill residuals; however, considerable care must be exercised to avoid plant upsets because of excessive loading of toxic materials or of large inflow surges of biodegradable matter. Permission to use a local sewage treatment plant for disposal of toxic material will probably be difficult to obtain unless the amount of material is small and toxicity is not a problem. Contracting the services of a private waste disposal firm that operates a biological treatment facility is a recommended option in those instances where discharge to a municipal sewage treatment plant is not possible. The cost of disposal by biological degradation ranges from essentially nothing (e.g., spill is simply allowed to drain to soil) to about $4 per m^3 (1.6¢/gal) of wastewater containing 200 mg/l BOD. This upper level of costs is based on a prefabricated 10,000 gpd (40 m^3/d) extended aeration activated sludge unit(26), with capital amortized at 10% over 5 years. This cost is equivalent to about $20 per kg of BOD disposed. Considerably less costly biodegradation operations are possible in lagoons or at land application sites where the cost of land is low. Land application is particularly attractive for waste oil disposal.(25)

Biodegradation of hazardous organic substances may not be practical in many instances because of very slow conversion rates or of toxicity problems. Acclimation of the biological culture to a particular organic substance may be necessary to achieve acceptable biodegradation rates. Certain classes of organic compounds are more resistent to biodegradation than others. For example, hydrocarbons--particularly, cyclic structures--and ethers are more resistant than alcohols, aldehydes, ketones, and acids. Biological oxidation data for many organic chemicals was reported by Heukelekian and Rand.(27) The relationship of biodegradability to chemical structure has been discussed by Ludzak and Ettinger.(28) Amenability to biological treatment is indicated for most of the organic compounds listed in Appendix A.

The selection of biodegradation for disposal will also be affected by the substrate materials with which spill residuals are associated.

Aqueous organic wastes are most readily treated biochemically. The presence of large quantities of solids, combustible or noncombustible, may cause difficulties with a given biochemical process. High solid loadings may interfere with settling processes or inhibit uptake and metabolism by active cell masses. In such cases, land application or a composting process could be preferable.

INCINERATION

General Description

As the environmental problems associated with many of the relatively cheap disposal options for hazardous wastes become increasingly evident, incineration has become the alternative of choice for destroying many organic hazardous wastes. The number and types of industrial waste incinerators are continually increasing.

Incineration is essentially a controlled oxidation process that is used to convert organic waste to CO_2, H_2O, and ash. Compounds in the waste containing sulfur, nitrogen, phosphorous, and halogens may also be oxidized to produce sulfur, nitrogen, and phosphorus oxides and hydrogen halides. The toxic or hazardous property of organic waste usually arises from the structure of the organic molecule as opposed to the properties of the elements that it contains. Therefore, destruction of the molecular structure to produce CO_2, H_2O, and inorganic oxides or halides eliminates the toxic or hazardous property. The existence of elements other than carbon, hydrogen, and oxygen (e.g., heavy metals) in the waste may result in the appearance of toxic materials in the ash or off-gas. The principal advantages to the use of incineration include:(29)

1. The basic process technology is available and reasonably well-developed.
2. The process is broadly applicable to most organic wastes and can handle large volumes.
3. Large land areas are not required.
4. The process is relatively rapid and not subject to upset due to toxic materials.
5. Operation is better understood than that for biological processes and therefore more easily optimized.

There are some generally applicable disadvantages:(29)

1. The equipment tends to be more costly and more complicated to operate than many other alternatives. Incineration facilities may not be conveniently located for periodic users.
2. The ash that usually results may or may not be toxic depending on the material incinerated so that incineration may not always be a means of ultimate disposal. In any case, the ash must be disposed.
3. Air pollution control equipment is required for treatment of the gaseous combustion products and of particulates.

Types of Incinerators

There are many types of incinerators that may prove adequate for destruction of most hazardous wastes. These will be discussed briefly in the following paragraphs. A more detailed discussion of the most applicable incineration methods is included in Appendix B.

Most incinerators currently used to burn hazardous materials are installed at industrial plant sites where the wastes are generated or at privately owned, central disposal facilities. The use of municipal waste incinerators to handle some hazardous wastes is being considered. Until recently, all hazardous waste incinerators have been land-based; however, hazardous wastes are currently being destroyed on specially equipped incineration ships in the North Sea and in the Gulf of Mexico and a mobile incineration system is under construction by EPA.

The various types of incinerators include open pit incinerators, multiple chamber incinerators, multiple hearth incinerators, rotary kiln incinerators, fluidized bed incinerators, liquid combustors, catalytic combustors, gas combustors, flares and molten salt incinerators. To the above may be added secondary abatement equipment, such as an afterburner device. Afterburners are themselves incinerators for completing the combustion of gases from the primary incinerators.

Open pit incineration has very limited application to the ultimate disposal of wastes and will not be considered further as a technique because of uncontrolled gaseous effluents. Note, however, that this technique has often been used for disposal of oil spill residues in remote locations and of certain waste explosives.

Multiple chamber incinerators are used for the disposal of solid wastes and are of two general types. The retort multiple chamber incinerator design is distinguished by the arrangement of chambers that forces the combustion gases to flow through 90 turns in both lateral and vertical directions. The in-line multiple chamber incinerator allows flow of the combustion gases straight through the incinerator with 90 turns only in the vertical direction. A capacity of from 50 to 750 lb/hr is the most efficient operating size for the retort incinerator. The upper limit for the use of the in-line incinerator has not been determined. When the moisture content of the combustible waste exceeds 10% by weight, supplementary gas burners are usually required. Multiple chamber units can be operated by one or two men and represent proven technology. Some of the wastes currently disposed of in multiple chamber units include general refuse, garbage, wood, paper, rubber, phenolic resins, wire coatings, acrylic resins, and polyvinyl chloride. The inability of the multiple chamber incinerator to handle gases, sludges, tars, and liquids limits its application in ultimate waste disposal operations. Multiple hearth incinerators have been utilized to dispose of sludges, tars, solids, gases, and liquid combustible wastes. This type of incinerator was originally designed to incinerate sewage sludges with low secondary fuel requirements, thus lowering operating costs when high water-content sludges were processed. The sludge or feed material parameters that control combustion are moisture content, volatiles content, inert content, and calorific value. The multiple hearth incinerator represents proven technology and is generally applicable to the disposal of combustible wastes. A diagram of a multiple hearth incinerator is presented in Figure 3.

The rotary kiln incinerator consists of a drum mounted at a slight angle from the horizontal on rollers to allow rotation in service (see Figure 4). The combustion chamber is lined with refractory materials to prevent damage to the steel shell. The rotary action during combustion leads to excellent mixing of solid or liquid burning waste and oxygen. Gases are normally not burned in a rotary kiln because the rotary action is not required for good mixing of oxygen and burning material during gaseous waste combustion. The length-to-diameter ratios of rotary incinerators vary from two to ten, depending upon the residence time needs of the combustible materials. Rotational speeds vary from 0.5 to 2.5 rpm. Combustion temperatures range from 870° to 1650°C, with solids residence time variations from minutes to hours. Efficient air seals and negative operating pressures assure that no leakage of toxic or noxious waste gases occurs. Sometimes a heat exchanger is used to preheat combustion air with realization of a significant increase in incineration capacity. The rotary kiln incinerator is generally applicable to the ultimate disposal of any form of combustible waste including explosives, chemical warfare agents, gases, sludges, and viscous liquids (tars) and represents proven technology.

Fluidized bed incineration is a relatively new technique for the ultimate disposal of solid, liquid or gaseous combustible wastes (see Figure 5). The bed is contained in a steel cylinder in which the fluidizing air enters from the bottom through a distributor plate, fluidizing a sand or inert bed above the plate. The waste material is injected into the bed above the distributor plate and combustion products leave at the top of the column. The sand bed acts as a heat sink, transferring heat to the combustible waste, which rapidly reaches ignition temperature and returns heat to the bed. The larger solid wastes remain suspended in the bed until combustion is complete. Ash fines are carried off in the gaseous combustion products to a scrubber or other processor before atmospheric discharge. Operating temperatures of from 760 to 870°C are reached initially with the aid of an auxiliary heater. Bed depths vary from 15 in. to several ft (1 m = 39.37 in.), depending on the desired waste residence time and pressure drop across the system. Gas velocities are usually from 5 to 7 ft/sec, with maximum velocity constrained by the size of the bed particles. The present limit in fluidized bed incinerator diameters is 15 m (50 ft). Large diameter solids must be shredded, pulverized or otherwise reduced in size, before addition to the bed to permit injection and even combustion.

The fluidized bed incinerator is generally suited to the ultimate disposal of a wide range of combustible materials. Gas temperatures are relatively low, minimizing the formation of nitric oxide, and excess air requirements as low as 5% reduce the size and cost of gas treatment

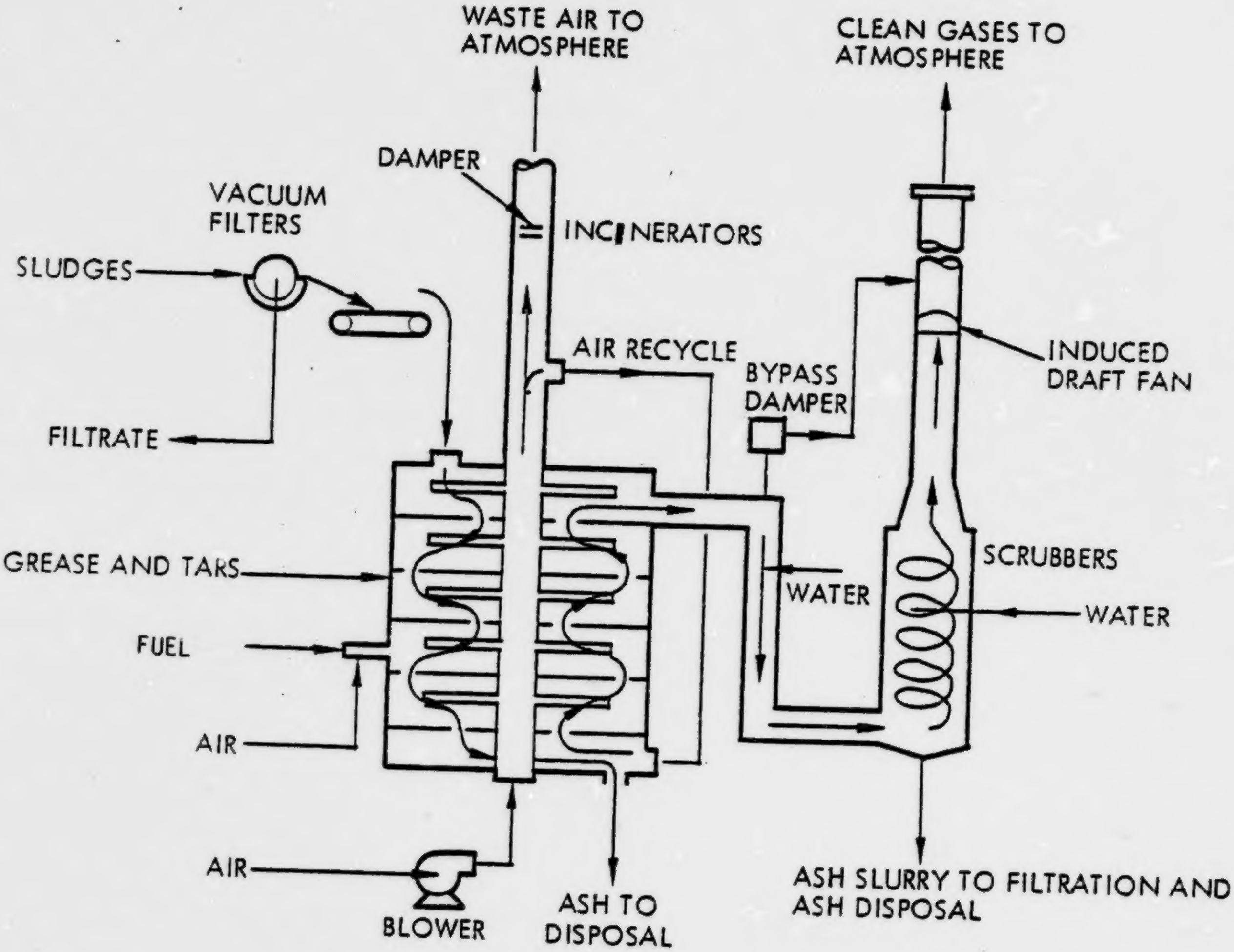

WASTE AIR TO ATMOSPHERE
CLEAN GASES TO ATMOSPHERE
DAMPER
VACUUM FILTERS
INCINERATORS
SLUDGES
AIR RECYCLE
BYPASS DAMPER
INDUCED DRAFT FAN
FILTRATE
GREASE AND TARS
SCRUBBERS
WATER
WATER
FUEL
AIR
AIR
BLOWER
ASH TO DISPOSAL
ASH SLURRY TO FILTRATION AND ASH DISPOSAL

FIGURE 3. Multiple Hearth Incinerator

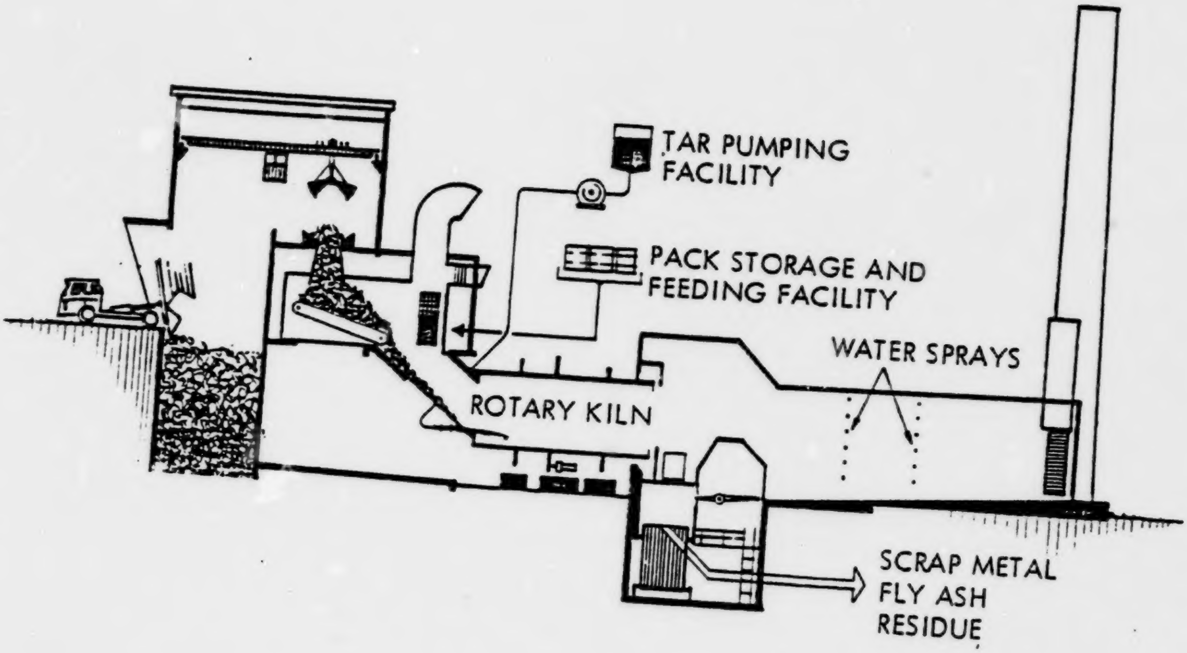

TAR PUMPING FACILITY
PACK STORAGE AND FEEDING FACILITY
WATER SPRAYS
ROTARY KILN
SCRAP METAL
FLY ASH
RESIDUE

FIGURE 4. Rotary Kiln Incinerator

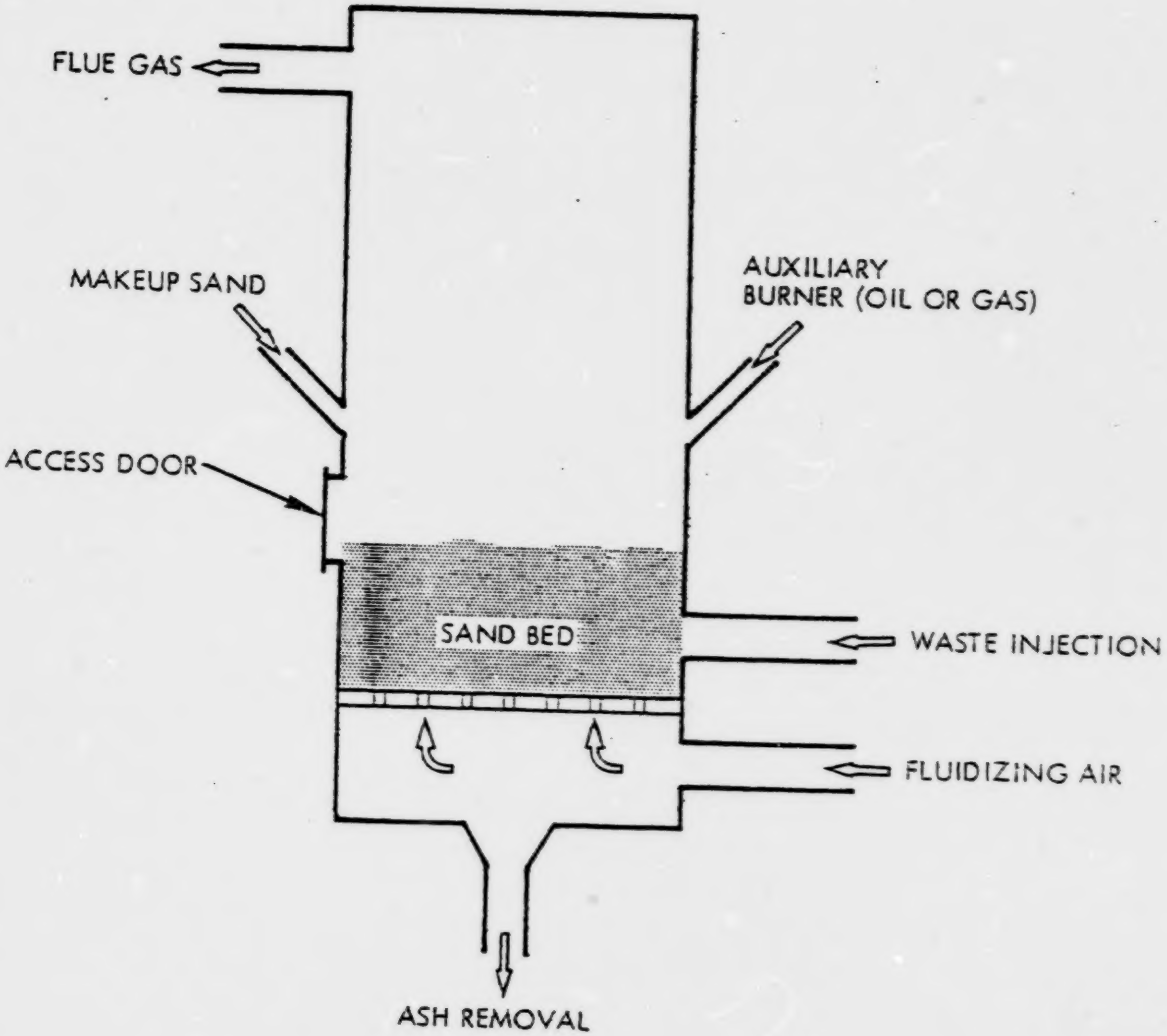

FLUE GAS
MAKEUP SAND
AUXILIARY BURNER (OIL OR GAS)
ACCESS DOOR
SAND BED
WASTE INJECTION
FLUIDIZING AIR
ASH REMOVAL

FIGURE 5. Fluidized Bed Incinerator

facilities. In addition, there are no moving parts in the region of highest combustion temperatures which should result in prolonged equipment life and ease of maintenance. The technology was first used commercially in the United States in 1962, so that it is a relatively new technology.

Liquid waste incinerators are widely used in industry (see diagram in Figure 6). When the heating value of a liquid waste is sufficiently high to support combustion, the material may be oxidized directly in a liquid waste combustor. Usually a specially designed burner is required. When the heating value of the waste is low, the waste is atomized with air or steam and injected into the flame of an auxiliary fuel-fired burner. The entering liquid is finely atomized to droplets less than 50 m in diameter in either two-phase nozzles or a pressure atomizer. Two-phase nozzles may be used to mix the air or steam and the fine droplets of liquid before entrance into the combustion chamber. When the liquid being burned is too viscous to be atomized in the nozzle, in-line heaters or addition of a miscible, lower viscosity liquid may be required to reduce viscosity. Liquid combustors require more turbulence and time for combustion to be completed than do gaseous combustors due to inherent liquid-air mixing problems. Care must be taken that undesirable reactions such as polymerization or nitration do not occur during heating of the liquid prior to atomization. Operating temperatures for liquid waste incinerators vary from 650 to 1650 C, depending on the feed autoignition temperature. Residence times vary from 0.5 to 1 sec. Liquid waste incineration is now used for the ultimate disposal of many industrial wastes including lubricating oils, polyester paint, solvents, polymers, resins, dyes, inks, latex paint, PVC paint, phenols, animal and vegetable oils, potato starch, various sludges, and chlorinated pesticide wastes.

Tar incinerators are a type of liquid waste combustor specifically designed for burning tars, contaminated solvents and sludges. Depending on the products of combustion of the waste material, the design may or may not include a secondary combustion zone. Tar combustors have been constructed to operate at specific temperatures from 980°C to 1930°C. At the highest temperatures, acid gases and fire brick corrosion may result. A wide variety of highly viscous tars and sludges can be handled by tar burner nozzles, but there are limitations that, when exceeded, will lead to the clogging of nozzles. Wastes exceeding these limitations (e.g., maximum allowable viscosity) are treated as solid wastes.

Catalytic incinerators are used for ultimate disposal of combustible wastes in low concentrations in a gaseous state. Catalytic oxidation is a more common name for the process used for the incineration of solvents and odiferous vapors from chemical and food processing. The effectiveness of catalytic materials is a function of reaction temperature, waste concentration, available oxygen, chemical composition, and geometric design of each catalyst unit. Poisons, suppressants, and fouling agents inhibit catalyst effectiveness. Vapors that contain metals such as mercury, zinc, lead, or their compounds generally reduce catalyst effectiveness ("poisoning"). A catalytic incinerator consists of a housing containing a preheater, when required, and a catalyst bed supported in such a manner as to expose a large surface area to the

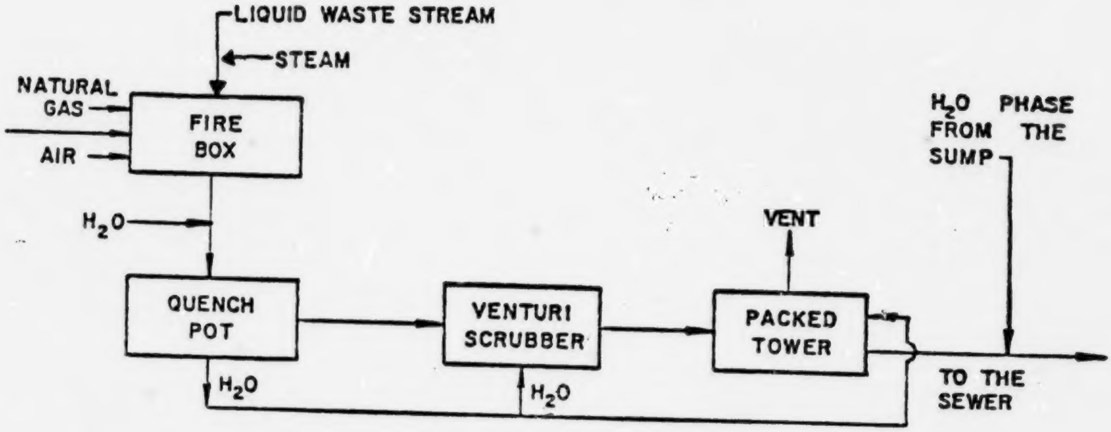

LIQUID WASTE STREAM
STEAM
NATURAL GAS
AIR
FIRE BOX
H₂O
QUENCH POT
VENTURI SCRUBBER
PACKED TOWER
VENT
H₂O PHASE FROM THE SUMP
TO THE SEWER
H₂O
H₂O

FIGURE 6. Flow Diagram of a Liquid Waste Incinerator

incoming gases. Gas velocities of about 6 m/sec (20 ft/sec) are commonly used.

The maintenance costs for catalytic incinerators tend to be high because of a gradual loss of catalyst activity through fouling or poisoning of the catalytic surface. Cleaning, regeneration, or replacement are often required.

Because the waste must have a low concentration and be in the gaseous or vapor state, catalytic incineration is usually conducted on the site of waste generation for odor and for toxic fume control in manufacturing processes using oils, asphalt, nitric acid, resins, paint, and coatings or involving roasting, rendering, and smoking. All of the hydrocarbons along with H_2S and CS_2, can be readily oxidized during catalytic incineration.

Gas combustors (direct-flame thermal incinerators) are used to dispose of combustible gaseous wastes that have a concentration usually less than 25% of the lower flammability limit. The gases are destroyed by a flame at temperatures of 480° to 815° C. A contaminated air stream containing the gaseous waste is injected into the burner throat along with fuel to create a flame. Combustion takes place in the combustion chamber with the effluent gases passing to a stack. Direct-flame incineration systems have been operated continuously at 90 to 99% efficiencies and are readily adaptable to thermostatic control. Residence times of from 0.3 to 0.5 sec are common along with gas flows of 4.6 to 7.7 m/sec. Direct flame incinerator applications work well in the resin industry, phthalic and maleic anhydride manufacture, food processing, grain drying, paint and varnish cooking, and carbon baking ovens.

Flares are basically pipes that discharge combustible gases to the atmosphere with a flame device and pilot light on the end of the pipe to ignite the gases. Oxygen for combustion is supplied from the surrounding atmosphere to promote burning. Steam is sometimes injected into the high volume gaseous stream to promote mixing. Flares are adversely affected by strong winds, often venting unburned hydrocarbons to the surrounding atmosphere or smoking due to incomplete oxidation of carbon particles. Other health hazards that can be found in the smoke include sulfur dioxide, when H_2S is present in the gas feed, and acidic effluents from halogenated hydrocarbons. Elevated flares are used to dispose of tank and reaction tower effluents while ground flares are used for the same purpose on an open ground space. Flares are generally useful for the ultimate disposal of large volumes of combustible gases, but have the problem of producing uncontrolled effluent gases and combustion products. For this reason, other types of incineration involving better effluent control are suggested for gases that can form noxious or toxic combustion products.

A special case of incineration technology, and a relatively new one,(32,33) is the ultimate disposal of organochlorine wastes at sea by incineration. German firms have constructed three ships especially outfitted for combustion operations. The Steel Plate and Construction Company situated in the Ruhr Valley outfitted the Matthais I in 1968 and the Matthias II in 1970. Burning operations have been carried out routinely in the North Sea area. In 1972, Ocean Combustion Services of Bremen outfitted the ship Vulcanus as an incineration vessel that could accommodate 4200 metric tons of waste. EPA tests of the combustion of organic chlorides containing 60 to 70% chlorine were concluded in 1974. A permit was subsequently issued, based on the favorable test results, and commercial burning operations began in the Gulf of Mexico. The feed waste included 1,2,3-trichloropropane, 1,1,2-trichloroethane, 1,2-dichloroethane, allyl chloride, dichloropropenes, dichlorohydrins, and dichlorobutanes. The incinerators employed were vertical liquid waste combustors about 5.2 m in diameter. In operation, fuel oil was used to preheat the combustion chamber to 1480 C. Then 20 to 25 tonnes/hr of the 3300 kg-cal/kg, high chlorine waste was fed to the combustion chamber whose temperature was adjusted to 1370 C. Excess air varied from 90 to 160%. The stack gases were emitted directly at about 1090 C and contained from 25 to 75 ppm CO, 5.2-6.2% HCl, and 200 ppm Cl or less. More than 99.9% of the toxic wastes were oxidized to relatively innocuous gaseous forms. The residence time in the incinerator varied from 0.5 to 1.0 sec. There are land-based incinerators that can easily duplicate these results, but emission controls are much more stringent for land-based operations.

The ocean burning permit issued in the above case was for specific organochloride wastes. Other types of wastes require testing before ocean burning can be evaluated as an ultimate disposal method.

Pyrolysis

Pyrolysis is a special incineration technique based on reacting or burning refuse solids with insufficient oxygen for complete combustion. Pyrolysis temperatures range from 500 to 800 C. Products include CO, CO_2, H_2O, H_2, N_2, CH_4, small quantities of other light hydrocarbons and char. The heating value of the resulting gas is usually between 880-3500 kg-cal/m^3 depending on whether air or oxygen is used. The gas is typically used as a fuel gas to replace natural gas. Pyrolysis units can be used for hazardous waste disposal; however, there are relatively few units in operation today and the secondary treatment faclities are typically designed for specific wastes. As a result, pyrolysis is not considered as a significantly important technique for hazardous waste disposal at this time.

Hazardous Waste Incineration

Incineration is most applicable to organic materials; however, certain hazardous inorganics can be rendered harmless by oxidation. A list of hazardous waste stream constituents for which incineration is considered an acceptable waste treatment alternative is contained in a report entitled Recommended Methods of Reduction, Neutralization, Recovery, and Disposal of Hazardous Wastes by the TRW Systems, Inc.,(35) for the Environmental Protection Agency. Reference to this source will provide an indication of whether a material in question may be incinerated and, in many cases, operating procedures, parameters, and problems will be outlined.

Generally, hazardous wastes that can be disposed of by incineration can be categorized in five groups, as below. The first three types of wastes may be in either solid or liquid form while the last two are self-explanatory.

1. Group I. Includes organic substances that contain only carbon, hydrogen with or without oxygen and/or nitrogen and oxygen (sometimes sulfur). The combustion products are clean and can be discharged to the atmosphere with minimal off-gas treatment.
2. Group II. Organic substances containing halogens, sulfur, phosphorus, and silicon. Chemicals such as carbon tetrachloride, vinyl chloride, ethyl bromide, PCB, chlorinated pesticides, and other halogenated materials appear in this group. Heating value of halogenated wastes depends on the halogen content and these wastes may or may not need an auxiliary fuel. The products of combustion will contain acids or oxides, which require air pollution control devices.
3. Organic/Metallic Wastes. Wastes that have metals or metallic compounds mixed with organic wastes, as well as organic wastes containing chemically bonded metals (organometallic compounds). When these wastes are oxidized, the combustion products will contain salts, which require that special attention be given to refractory selection, oxidation temperature, and residence time. Auxiliary fuel is often required for complete oxidation of these materials. Sub-micron particulates and mists in the product gas will require secondary gas treatment equipment.
4. Aqueous Wastes. Any or a combination of the above wastes in a solution of greater than 60% water. Because of the low heat of combustion, this group of wastes do not support combustion in a burner and require an auxiliary fuel.
5. Solid Wastes. Any or a combination of the above wastes adsorbed onto, absorbed into, or mixed with a nonhazardous solid material. This group includes such items as contaminated adsorbents; sludge from waste water treatment; sawdust, straw, and other absorbents used to clean up hazardous materials spills; residual material from a spill cleanup; whole capacitors containing PCB; and "empty" pesticide cartons and containers.

Liquid organic wastes can usually be incinerated simply and easily in a liquid combustor providing their viscosity is low enough (750 ssu or less) for proper atomization. A thermal vortex burner (see Figure 7) is reported to work well in this application.(34) When proper operating conditions are maintained, organic wastes can be completely oxidized.

Liquid halogenated wastes, when their heating value is sufficiently great, may be oxidized in the same manner as organic wastes. Wastes with high halogen content (60-70% chlorine by weight) require auxiliary fuel. In this case, the waste is atomized by steam or air and injected into the flame zone of the burner just beyond the exit of the burner combustion chamber. Halogens and hydrogen halides will be present in the combustion gases. Hydrogen halides can be removed by conventional wet scrubbing techniques; however, halogens are more difficult to handle. As a result, hydrogen or methane is often added to the combustor to assure complete conversion to halides.

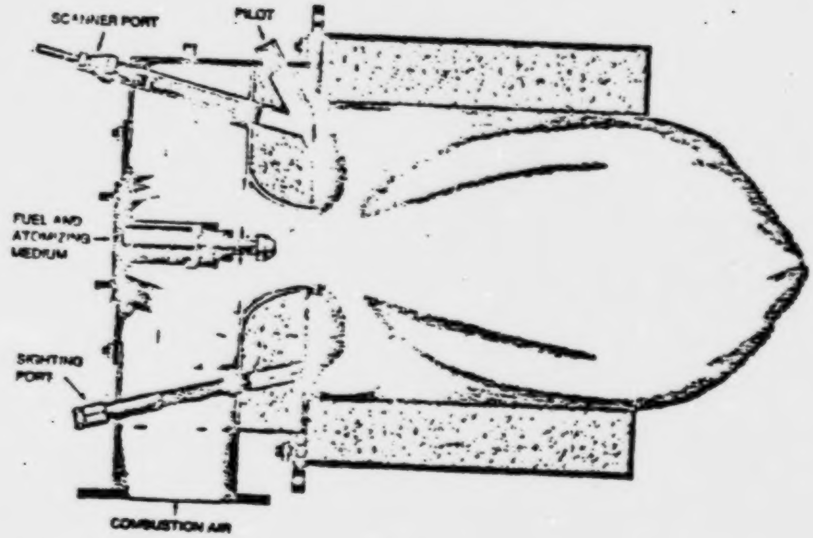

SCANNER PORT
PILOT
FUEL AND ATOMIZING MEDIUM
SIGHTING PORT
COMBUSTION AIR

FIGURE 7. Thermal Vortex Burner(34)

Liquid organic/metallic wastes and aqueous wastes, which do not support combustion and thus require an additional fuel, may be atomized and injected into the flame zone of the burner. Aqueous wastes are often preconcentrated to reduce secondary fuel costs. Materials containing toxic heavy metals should not be incinerated unless the fate of the metal components is known and can be satisfactorily controlled by pollution control equipment. Some of these metals may end up not only in the ash but in the gaseous combustion products as well.

Combustion of solid wastes and organic, halogenated, and metallic wastes in solid form is not so straightforward. Incineration of solid hazardous wastes has not generally been considered an acceptable means of disposal because most of the solid type incinerators in existence were municipal refuse incinerators, which did not operate at conditions appropriate for destruction of hazardous wastes and did not have suitable air pollution equipment.

Rotary kiln incinerators specially designed for waste disposal have been used successfully to incinerate many types of hazardous solid wastes including explosives and chemical warfare agents.(35) Recently PCB-containing capacitors and nitrochlorobenzene wastes were incinerated in a commercial-scale rotary kiln incinerator with 99.999% destruction efficiency.(36) A rotary kiln incinerator was used to incinerate sewage sludge contaminated with Kepone and Kepone wastes. Destruction efficiencies of 99.999% were achieved.(37) Rotary kilns are used by industry to dispose of refuse consisting of plastics, wood, paper, and other combustible material including hazardous chemical wastes. Generally, rotary kiln incinerators designed for waste disposal and equipped with suitable pollution control equipment can be considered an acceptable means for disposal of hazardous solid wastes; however, this type of facility is not readily available in many areas. A map giving the location of rotary kiln, liquid, and other types of hazardous waste incinerators is presented in Figure 8 (Ref 35).

The newer sludge incinerators that utilize fluidized bed or multiple hearth technology adapted from other industries are potential systems for hazardous solid waste disposal. These new facilities can often be operated at conditions acceptable for hazardous waste destruction and are usually equipped with suitable air pollution equipment. The large number of these types of incinerators make them particularly attractive. Tests were recently performed with DDT, 2,4,5,-T, and PCB to determine whether these materials could be coincinerated with sewage sludge in a multiple hearth incinerator.(38) In these tests, concentrations of the hazardous waste material ranged from 2 to 5% based on dry sludge weight. Destruction efficiencies were 99.99+% for DDT, 99.97+% for 2,4,5,-T, and 94% for PCB. The lower destruction rate for PCB may have resulted from the configuration of the incinerator used. The sludge was fed through the top hearth, and it is conjectured that some of the volatile PCB's were vaporized directly into the gaseous exhaust and were discharged from the incinerator before being oxidized.(39)

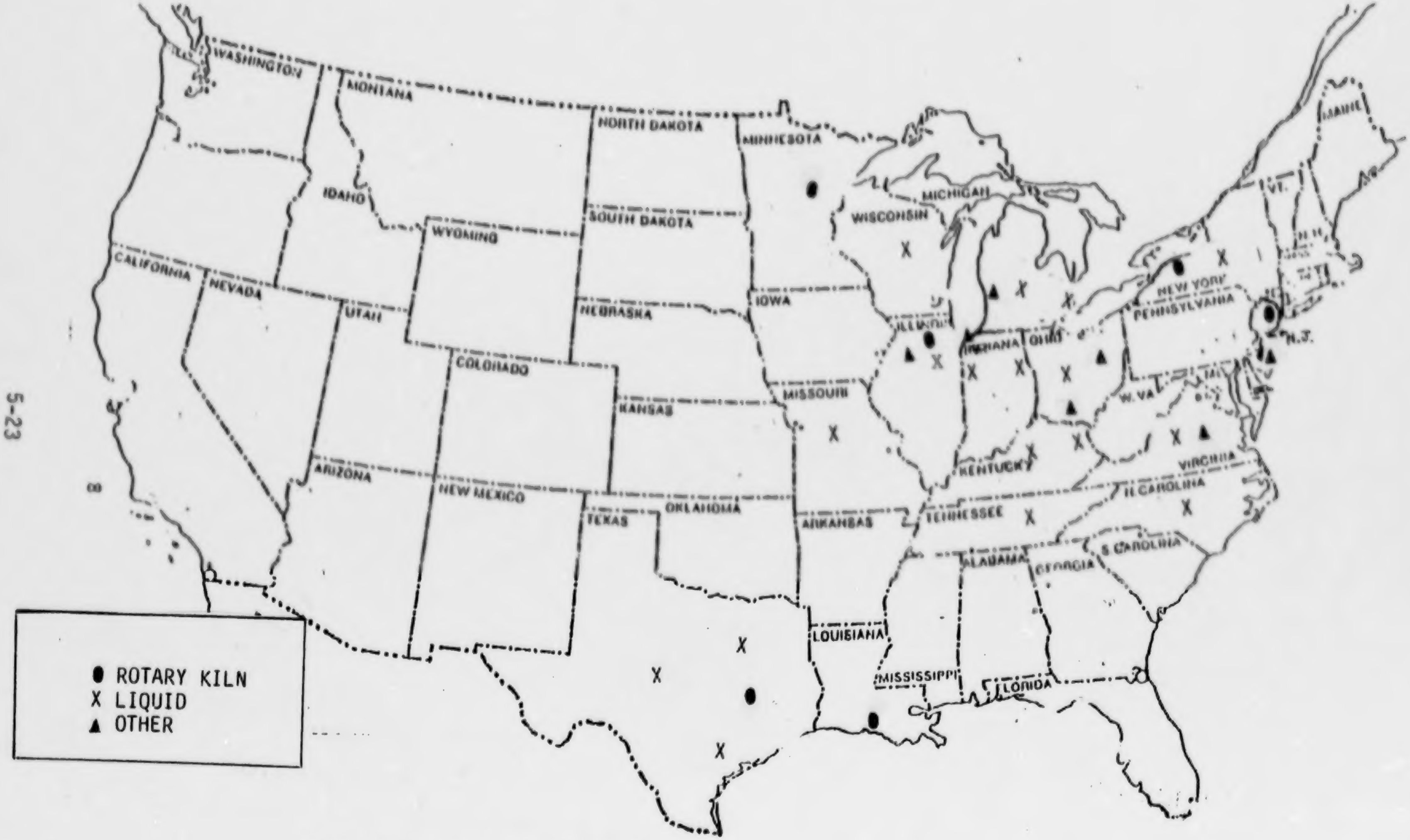

● ROTARY KILN
X LIQUID
▲ OTHER
WASHINGTON
MONTANA
NORTH DAKOTA
MINNESOTA
IDAHO
SOUTH DAKOTA
WISCONSIN
MICHIGAN
WYOMING
CALIFORNIA
NEVADA
UTAH
NEBRASKA
IOWA
ILLINOIS
INDIANA
OHIO
NEW YORK
PENNSYLVANIA
N.J.
VT.
N.H.
MAINE
COLORADO
KANSAS
MISSOURI
W. VA
KENTUCKY
VIRGINIA
ARIZONA
NEW MEXICO
OKLAHOMA
TEXAS
ARKANSAS
TENNESSEE
N CAROLINA
S CAROLINA
ALABAMA
GEORGIA
LOUISIANA
MISSISSIPPI
FLORIDA

FIGURE 8. Location of Hazardous Waste Incinerators in the United States

The five types of incineration generally employed for destruction of toxic organic water are illustrated in Table 2, which also shows the types of feed materials that each is capable of processing.(41) Successful application of incineration requires accurate and reliable information about the composition and characteristics of the waste to be processed.

Specifically, for waste to be incinerated, the following are determined initially:(42)

- heat content
- acid scrub requirement (elemental composition)
- ash content
- specific gravity.

Other evaluative or process control tests, such as burn rate, are conducted later and are based on the initial test results.

As a general rule most organic hazardous materials can be virtually destroyed in an oxygen-rich atmosphere at 1000°C at a dwell time of 2 sec.(29) Many are completely destroyed at lower temperature/dwell time conditions but some (e.g., DDT, PCB's) require more rigorous conditions. Proposed RCRA regulations specify a temperature of 1200°C for 2 seconds for chlorinated aromatic hydrocarbons (5). Proposed operating criteria for destruction of PCB's are 1200°C with a 2-second dwell time and 3% excess oxygen.

Assessment

Incineration is a widely applicable and reasonably well-developed method for hazardous waste disposal. When undertaken with proper air pollution control equipment, incineration can be used to completely destroy approximately 60% of the hazardous materials listed in Appendix A with little or no affect on the environment. This includes all hydrocarbons, halogenated organics, and organics containing nitrogen, oxygen, and sulfur. (Incineration is not always classified as an ultimate disposal method since any hazardous (heavy metal) or nonhazardous ash resulting from incineration must be disposed of separately.) Organometallic wastes can also be handled by incineration; however, special consideration must be given to the selection of refractory liners and to air pollution control equipment design. Note that the resulting ash may contain hazardous metallic compounds.

The cost of incineration varies with the type of incinerator and the waste material. Typically, costs range from $9 to $31/tonne of waste for solid incinerators (fluid bed, rotary kiln, and multiple hearth units) and $0.26 to $26/m^3 for liquid combustors.(35) These are total capital and operating costs for the year 1973. Capital costs are around 75% of the total.(35)

These costs do give an incomplete indication of the true cost of disposal of hazardous materials from a spill or release. The total cost of disposal depends on the type of spill (cost of spill cleanup and preparation for incineration) and the location of the spill (transportation costs to the incinerator).

TABLE 2 PROCESSING CAPABILITIES OF FIVE TYPES OF COMMONLY USED INCINERATORS

Process	Waste Form		
	Solid*	Liquid	Gas
Rotary Kiln	X	X	X
Fluidized Bed	X	X	X
Multiple Hearth	X	X	X
Liquid Injection		X	
Pyrolysis	X		

* = Size reduction may be necessary
X = Acceptable

Most incinerators that routinely burn hazardous wastes are located at industrial plant sites or privately owned, central disposal facilities. The number of these facilities, while growing fast, is small. It is not likely that one of these units would be convenient or available to handle waste material from a spill.

There are a large number of newer sewage sludge incinerators using fluid bed or multiple hearth technology with suitable air pollution equipment that could be used for destruction of hazardous material from a spill or release.

In general, incineration is the most effective means of destroying a wide range of hazardous materials with the smallest impact on the environment and is the method of choice for disposal of nonbiodegradable and highly toxic organics. However, incineration is more costly than other disposal methods such as biological treatment and landfilling, and properly equipped facilities are not readily available for periodic users. Availability is limited further since individual incinerator types cannot necessarily handle all substrate forms. Hence selection of a unit must be based on a number of factors:

- proximity;
- design criteria as compared to the operating parameters required for the hazardous material involved;
- ability to handle the substrate form; and
- capacity.

NEUTRALIZATION

Description of Process

Neutralization may be defined as adjustment of the pH of a solution to a level between 6 and 9. Neutralization to this pH range normally renders an aqueous solution safe to discharge to receiving waters or soils with respect to hydrogen ion concentration. There are a number of methods available to effect the neutralization of acidic or caustic solutions.(43,44) Lime slurries and solutions of caustic soda (NaOH) or soda ash (Na_2CO_3) are commonly employed by industry to neutralize excessive acidity. Excessive alkalinity is generally neutralized by the addition of sulfuric or hydrochloric acid solutions or by sparging flue gas(or CO_2) through the solutions. Controlled addition of these reagents is required, except in the case of CO_2, to avoid adding excessive amounts and overshooting the desired pH range. Controlled addition is generally accomplished in a tank where the treated solution can be easily monitored for pH with the aid of a pH meter or color indicators. A spill of acid or caustic material outside such a controlled environment cannot be neutralized as easily. The recommended approach to in situ neutralization is the use of weakly acid or weakly basic materials for neutralization of alkaline and acidic spills, respectively.(45) Powdered limestone ($CaCO_3$) and baking soda ($NaHCO_3$) are excellent reagents for neutralizing acid spills. Both of these reagents are capable of neutralizing acid without exceeding the pH 9 limit. Furthermore, the cessation of CO_2 evolution when additional quantities of these reagents are added to a spill indicates completion of the neutralization reaction.

Neutralization of caustic spill residuals with CO_2 would be the best approach to neutralizing excessive alkalinity from an environmental viewpoint; however, in situ application of CO_2 may be difficult in most instances. Alternate commonly available weakly acidic reagents include acetic acid, aluminum sulfate (alum), sodium mono- or di-hydrogen phosphate, and ferrous sulfate (copperas). Acetic acid has the disadvantage of contributing BOD to receiving waters and aluminum or ferrous sulfate can add metal ions and excessive acidity when more than the stoichiometric quantity is used. Phosphates are nutrients for biological systems and high levels may be undesirable.

Neutralization is frequently used as a pretreatment step to effect the precipitation of a toxic ion such as Cr^{+3}. The ultimate disposal method used in this case may be disposal of the hydrous chromic oxide in a secure landfill. Lime is also used in a like manner to neutralize excessive acidity while precipitating toxic or undesirable anions such as fluoride, arsenate, and phosphate.

Assessment

Neutralization is considered as an ultimate disposal step only for those acids and alkalies that can be rendered nonhazardous by this method. Common hazardous materials included in this category are listed below:

calcium hydroxide
calcium oxide
hydrochloric acid
nitric acid
potassium hydroxide
sodium hydroxide
sulfuric acid

Neutralization of the acids listed above with either sodium bicarbonate or powdered limestone will result in nonhazardous reaction products that can generally be flushed away with water. The use of sodium bicarbonate is preferred in those instances where some mixing is required to achieve effective neutralization. Sodium bicarbonate is soluble in water and can be distributed more rapidly throughout a solution or a porous mixture such as soil contaminated with acid. Good mixing normally occurs as a result of CO_2 evolution in shallow pools or layers of acid solutions treated by broadcasting solid sodium bicarbonate or powdered limestone over the affected areas. Limited quantities of sodium bicarbonate in the form of baking soda are available for small acid spills from grocery stores at approximately 50¢ per pound. Powdered limestone can generally be obtained from local agricultural product outlets at costs under 10¢ per pound. Both sodium bicarbonate and powdered limestone are quite safe to handle. Substrate form will have little impact on neutralization processes other than direct increases in reagent requirements. For instance, some soils may exhibit acid or alkaline properties, which would augment chemical requirements. More often, however, soil and other substrates will have buffering properties that could reduce reagent requirements.

PRECIPITATION

Description of Process

Precipitation in liquid medium is the formation of an insoluble or sparingly soluble substance that is brought about by a chemical reaction, a change in temperature, or--in the case of a supersaturated solution--the introduction of seed crystals. Precipitation can serve to separate a hazardous constituent from a solution to reduce the quantity of hazardous material to be managed. Furthermore, precipitation can also render the hazardous material much less soluble, which reduces its potential for migration from a disposal site. Under the proper conditions, a precipitate containing a hazardous constituent may have a solubility low enough to no longer qualify the material as hazardous when a leach test is applied. Precipitation of chromic hydroxide is an example of the formation of a sparingly soluble compound from a solution of a hazardous heavy metal ion. Precipitation of chromic hydroxide by treatment with lime is commonly performed with waste solutions containing Cr^{+3}:

$$2\ Cr^{+3} + 3\ Ca(OH)_2 = 2\ Cr(OH)_3 + 3\ Ca^{+2}$$

The precipitated chromic hydroxide can be separated from the wastewater by sedimentation and filtration. In the absence of other effects (e.g., solubilizing effect of chelating agents) the solubility of chromic hydroxide in water at pH 5 is 2×10^{-11} mg/ , which will give a Cr^{+3} concentration that is orders of magnitude less than the 0.5 mg/ limit proposed for this metal in a leach test at pH 5.

Treatment of heavy metal salt solutions with alkaline reagents is commonly used to precipitate the hydroxides of these metals.(46,47) However, one should be aware that not all heavy metal hydroxides will qualify as nonhazardous with a pH-5 leach solution. Cadmium and lead hydroxides, for example, are sufficiently soluble to exceed the proposed RCRA limits. Nevertheless, hydroxide precipitates of heavy metals are useful to minimize the mobility of these hazardous substances in a secure landfill.

Spill residues of many of the heavy metal salts listed in Appendix A will not qualify as hazardous waste under currently proposed RCRA guidelines. Salts of zinc, iron, copper, cobalt, and nickel, for example, would be exempt unless associated with acidity or alkalinity outside the pH 3 to 12 range or with other hazardous constituents (e.g., cyanide). However, protection of the environment from mobile species of these heavy metal ions is needed and precipitation treatment of spill residues in solution will serve a useful purpose in many instances. The precipitated hydroxides of zinc, iron, copper, cobalt, and nickel may be disposed in a suitable sanitary landfill depending on local conditions and regulations.

In addition to hydroxide precipitates, other heavy metal precipitates such as carbonates and sulfides may be used to prepare sparingly soluble compounds of these metals. Cadmium carbonate, for example, is less soluble than cadmium hydroxide. Some of the sulfide precipitates of heavy metals also exhibit very low solubility (e.g., mercuric sulfide). The use of sulfide as a precipitating agent involves careful control to avoid an overdose, which will in itself be toxic. Furthermore, heavy metal sulfides are prone to oxidize in the presence of moist air and to release the heavy metal in dilute sulfuric acid solution.

Precipitation may also be used as a scavenging process for removing dilute hazardous metal ions from solution. Ferric hydroxide scavenging of low concentrations of arsenic is an example.(48) Low concentrations of other heavy metals in solution can frequently be "carried down" on a dense floc of ferric or aluminum hydroxide. The sludges formed by scavenging may or may not qualify as hazardous waste depending on the amount and solubility of the hazardous metal scavenged.

Assessment

Precipitation of metal ions designated as hazardous under proposed RCRA guidelines (i.e., As, Ba, Cd, Cr, Pb, Hg, Se and Ag) will probably serve as a pretreatment step only and final disposition of the sludges formed will be in a secure landfill. Under optimum conditions, however, the solubility of these metals can be reduced by precipitation to the level where the precipitate would not be designated as hazardous. In this case it would not be necessary to rely on a secure landfill to prevent dispersion to the environment.

Common chemical reagents that can be used to effect hydroxide precipitation of heavy metals include lime, soda ash, sodium bicarbonate, powdered limestone, and sodium hydroxide. As in the case of neutralization, in situ precipitation would best be accomplished with powdered limestone or sodium bicarbonate since these reagents are least likely to cause environmental damage if used in excess of the amount needed to effect environmentally acceptable precipitation of the metal ion. If possible, containment of spills of highly toxic metal salts should be attempted in order to facilitate recovery of the sludge formed by precipitation. Transfer of solutions containing spill residues to treatment vessels, either makeshift in the field(43) or at a treatment facility, provides a better means of recovering the sludge than--for example--in situ treatment of an impounded stream.

Precipitation of heavy metals is likely to occur in the case of spills on soil, especially alkaline soil. The neutralizing quality of soil will cause the precipitation of heavy metal hydroxides or hydrous metal oxides. In the case of low toxicity metals such as iron and aluminum, this natural action will serve as a useful approach in many instances. Precipitation in the soil may be enhanced by a water wash to disperse the metal salts or by treatment of the affected area with a suitable alkaline reagent or by a combination of both.

It is anticipated that precipitation will be widely used as a method to dispose of certain hazardous material spill residuals or as a pretreatment step to prepare a sparingly soluble compound of a hazardous substance for disposal in a secure landfill. The reagents and equipment for a precipitation process are readily available in most locations and the process is relatively simple to carry out and monitor. Precipitation is limited to a small fraction of the materials listed in Appendix A; however, some of these such as iron and aluminum salts are widely used in commerce.

CHEMICAL OXIDATION AND REDUCTION

Description of Process

Chemical oxidation or reduction is an effective method for converting certain types of hazardous reducing or oxidizing materials to less hazardous or nonhazardous materials.(43,44,49-51) In the latter case it is considered as an ultimate disposal method by itself. Redox reactions are perhaps more frequently used as a pretreatment step to produce a less hazardous material as in the case of reduction of very toxic Cr^{+6} to less toxic Cr^{+3}, which can be precipitated as chromic hydroxide.

A variety of chemical reagents are available for the oxidation of selected hazardous materials; and the choice of a particular oxidant usually depends on: the oxidizing power needed, safety, cost, and availability. Oxidants frequently employed for treating hazardous wastes include: sodium and calcium hypochlorite, chlorine gas, ozone, and hydrogen peroxide. Electrolytic oxidation is also used by industry; however, electrolysis has very limited utility in the field, as does the use of chlorine gas or ozone, which also require special application equipment. Sodium hypochlorite, calcium hypochlorite, and hydrogen peroxide are widely available and merit first consideration for in situ spill treatment or make-shift field treatment units. Oxidation of highly toxic cyanide with chlorine gas or hypochlorite salts is a classic example oxidation of a hazardous material to innocuous end products, e.g., CO_2, N_2, and H_2O. Care must be exercised to avoid overuse of chlorine or reagents containing hypochlorite since these are highly toxic to aquatic organisms. Hydrogen peroxide is a useful oxidant that has a low toxicity when diluted.

Chemical reductants that are widely available include ferrous sulfate, sulfur dioxide, and sodium sulfite. Sulfur dioxide is a gas at ambient temperatures and would be difficult to apply in most field situations.

The reduction of very toxic Cr^{+6} to Cr^{+3} represents one of the most important oxidation/reduction reactions. Chromates and dichromates are widely used in the metal plating industry, in cooling tower water conditioning, in the textile industry as mordants, in pigments with barium, lead, molybdenum, and zinc compounds, in chrome tanning operations as sodium dichromate and in the photographic industry (often as ammonium chromate or bichromate) for accelerating development and for hardening gelatin and in the manufacture of lithographic plates.

Two disposal methods are now practiced for Cr^{+6} compounds. Both methods reduce the Cr^{+6} to Cr^{+3} by addition of SO_2, flue gas, sodium sulfite or metabisulfite, iron filings or brass or aluminum turnings from machining operations. Where the Cr^{+3} concentration is very low it may be directly disposed to the sewer. In the case of high Cr^{+3} concentrations, the solution is pH-adjusted to 9.5 and the metal hydroxide is precipitated. The chromium hydroxide sludges are, however, high in water content (80% H_2O by volume) and require settling over long time periods before disposal to a proper landfill operation.

Destructive chlorination or chlorolysis of organics can be considered as a chemical oxidation technique. However, the carbon tetrachloride product usually obtained by chlorolysis of organics is also a hazardous material.

Assessment

Chemical oxidation or reduction is an ultimate disposal process that should be used for the following hazardous materials whenever practicable:

cyanides
hypochlorites
chlorates
sulfides
sulfites
chromates
permanganates
peroxides
hydroxylamine
nitrites

Reducing hazardous materials such as cyanides, bisulfite, sulfite, bisulfide, sulfide, hydroxylamine, nitrite, and sulfur dioxide can be oxidized to nonhazardous substances with chlorine or hypochlorites. Care must be exercised in using hypochlorites or chlorine to avoid an excess. Solutions containing 5% sodium hypochlorite (common bleach solution) are readily available at grocery stores at about $0.40 per liter. The use of hydrogen peroxide may be preferable for the oxidation of sulfides, bisulfides, sulfites, bisulfites, and sulfur dioxide. Sodium sulfite or bisulfite are recommended reducing agents for hazardous oxidizing materials such as hypochlorites, chlorine, hydrogen peroxide, and permanganate. Variations in substrate materials will have little effect on this process other than to change overall reagent requirements. For instance, the presence of large amounts of organic solids could greatly increase the demand for oxidizing agents in an oxidation process.

LOW-TEMPERATURE FIXATION

Description of Process

The disposal of toxic liquids or sludges into land disposal sites can lead to problems with groundwater contamination from leaching by natural precipitation and airborne contamination from windblown dust. Low temperature fixation of wastes by mixing with asphalt, sulfur, tar polyolefins, or epoxy resins encapsulates the wastes and prevents them from leaching by rain water or dispersion by wind. Organic binding agents are primarily hydrophobic in nature and many of them do not function well in a high moisture environment. These agents also suffer from ultraviolet light and microorganism instability. Inorganic solidification systems using various silicates in conjunction with proprietary constitutents have been developed by several companies in the United States.(52,53) These solidification processes have been applied to the ultimate disposal of SO_x power plant scrubber sludges.(54) Sulfate sludge is fixed in two steps taking up to 72 hr. The first produces alkaline earth sulfate or sulfite compounds, usually typified by a fibrous gypsum. The second reaction involves cement-like reactions between fly ash alumina and silica, lime compounds and sulfur oxide salts.

For fixation, the SO_x sludge can be dewatered and mixed with dry fly ash without any other additives . Soluble silicates and silicate-setting agents can also be used to solidfy a wide range of liquid and sludge wastes. The solids from the above processes are reported to have permeability coefficients on the order of 10^{-6} to 10^{-7} cm/sec (at 10^{-6}, water nominally takes 1 year to penetrate 30 cm).(55) Consequently, leach rates of metals and other toxic inorganic materials contained in the original sludge or liquid are very low. Long-term leaching results for the cited fixation products are lacking. Extensive leaching tests have shown that the leaching rates are generally low for these solids although all do leach pollutants to some degree and may disintegrate as a result of weathering. Electroplating sludge used by Mahloch(56) in his testing program showed that leaching characteristics of the solids as compared to the raw sludges were a function of the ion that has been fixed. Calcium, for example, showed little difference between leach results on the raw sludge and three different solidification-process solids. Cadmium, on the other hand, leached at a much slower rate for all three solids than for the raw sludge.

Wiles and Lubowitz(57) described a process that uses polybutadiene as a binder resin for encapsulating dry hazardous wastes. The process consists of dewatering the waste, coating the particulates with polybutadiene resin in a solvent, removing the excess solvent, agglomerating the resin-coated particulates by compaction, and curing the thermosetting material, which may then be jacketed with polyethylene into 230 to 460 kg blocks of waste. About 4 wt% of polybutadiene was required for coating and binding waste particulates. The amount of polyethylene used depends upon the desired jacket thickness. Immersion of several encapsulated wastes in distilled water, seawater NH_4OH citric acid, HCl, and NaOH for up to 120 days showed minimal leaching of heavy metals (Cu, Cr, Zn, Cd, and Hg) and calcium but somewhat greater leaching of sodium. Monosodium methane-arsenate encapsulated by this process leached less than 0.01 mg/L, as after 80 days in distilled water and 1.5 m NH_4Cl. The cost of the process was estimated at $100/dry metric ton (tonne) of waste (4 wt% polybutadiene coating and binder and a 0.64-cm thick polyethylene jacket on a 360 to 460 kg waste block). Yearly throughput of 18,000 tonnes and the use of commercial resins was assumed in the cost estimate. The authors point out that, though the process is expensive, there are very few alternatives that allow ultimate disposal of toxic inorganic wastes, such as arsenic, in a landfill operation.

Replacement (substitution) reactions of one cation for another in a mineral (say Ba^{++} for CA^{++} in apatite, which is relatively insoluble (58)) is one approach for fixing heavy metals. Apatite ($Ca_5(OH)(PO_4)_3$) may be formed as follows:

$$NaOH + 3\ Na_3PO_4 + 5\ CaCO_3 \rightleftharpoons Ca_5(OH)(PO_4)_3 + 5\ Na_2CO_3.$$

The $CaCO_3$ can be placed in a column and the Na_3PO_4 added to the influent. Approximately 38 mg/L PO_4^{-3} are required for the reaction to proceed. As the replacement occurs, barium and other cations that fit into the forming apatite crystal structure are removed from solution into the relatively insoluble apatite. Very high decontamination factors between column influent and effluent are possible.

Fixation processes have generally focused on containment of inorganic species. A few fixation agents appear to be effective for organic substances. Epoxy resin and polymeric sulfur binders, for example, were useful in reducing the leachability of Kepone-contaminated sediments.(59) Polymeric silica cements were not effective since the higher alkalinity of these cements tends to solubilize the Kepone.

Assessment

Fixation processes, which convert hazardous materials to nonhazardous materials by reducing the leach rate to an acceptable level, are reviewed as ultimate disposal methods although actual disposal may take place in a sanitary landfill. Heavy metal sludges containing the hydrous oxides of Fe, Ni, Cu, Zn, and Co fit in this category; however, final determination of utility must await the development of landfill disposal standards. Little work has been done on fixation of organic wastes and that alternative is not recommended at this time. In this report, fixation processes that convert hazardous materials to less hazardous forms are considered to be pretreatment methods. In this report, deposition of the fixed waste in a secure landfill is classified as the ultimate disposal method.

Fixation agents must be selected carefully, usually through screening tests. This is particularly true for the disposal of complex mixtures such as spill residuals. The presence of trace contaminants can greatly affect the integrity of the stabilization product. For instance, organic materials have long been known to reduce the strength and longevity of concrete and to enhance weathering. Concrete is analagous to the Portland Cement-based fixation mixtures. Similarly, some inorganic salts can prevent a good set. Consequently, preliminary testing of proposed agents is necessary, and long-term evaluation is advisable.

SANITARY LANDFILL

Description

A sanitary landfill can be defined as a land disposal site employing an engineered method of disposing of solid wastes on land in a manner that minimizes environmental hazards by spreading the wastes in thin layers, compacting the solid wastes to the smallest practical volume, and applying cover material at the end of each operating day. Landfills occupy a niche between the surface disposal of wastes such as for sewage sludges and the deep burial or geologic storage of extremely hazardous wastes.

Landfill operations are characterized by the two functions of maximum utilization of the soil adsorptive properties and the storage of wastes in a manner to promote isolation from man and his environment. Some liquids and slurries have been disposed into landfills, but the potential for leachate migration exists even in well-designed and operated sanitary landfills. Study and selection of a landfill site minimizes use hazards although the escape of hazardous gases such as cyanide always is possible through the indiscriminate mixing of wastes. Certain wastes such as soluble heavy metals, salts, and other water soluble, toxic material should not be disposed to sanitary landfills. Additional precautions over and above those taken during sanitary landfilling of municipal solid wastes are required for ultimate land disposal of hazardous wastes. The sanitary landfill should be limited to disposal of inert solid wastes (nonhazardous) that do not constitute a threat to the water quality of adjacent areas. Examples of the types of wastes that might be disposed to a sanitary landfill include calcium sulfate-calcium fluoride wastes from the fertilizer industry and slag from some smelting operations if the slag is in the form of a glass containing no soluble heavy metal compounds. Codisposal of industrial wastes with municipal wastes in sanitary landfills has caused problems. Consequently regulatory agencies in the early 1970's initiated campaigns to segregate these wastes.(60) The high organic content of municipal solid waste results in biodegradation processes that can lead to solubilization and subsequent migration of heavy metals, for example. Indiscriminate mixing of solid wastes can also cause chemical reactions that are detrimental to containment of the wastes. Sanitary landfills were reviewed by Liptak(61) in relation to site selection and preparation, environmental impacts, and utilization.

Assessment

Sanitary landfills represent one of the most widely used ultimate disposal methods currently practiced in the United States. The use of sanitary landfills for burial of anything is presently diminishing to some extent as communities recognize the problems associated with burial of some types of hazardous materials at these sites. Nevertheless it is expected that sanitary landfills will continue to be extensively used for hazardous spill residuals which can be disposed via this route. The latter determination will depend heavily on pending hazardous waste regulations, which may preclude this option entirely. Materials amenable to this method of disposal include materials that are not designated as hazardous by regulatory agencies and would not be a potential problem in a sanitary landfill. Vegetable oils and relatively innocuous inorganic salts such as sodium phosphate and aluminum chloride or sulfate are examples of materials which could be placed in a sanitary landfill. Large volumes of soil or other inert substrates contaminated with low levels of spill residuals would also be likely candidates for sanitary landfill disposal. From a technical viewpoint little or no impact on the environment surrounding the landfill would be anticipated since normal usage of the landfills would far overshadow the infrequent use of a particular sanitary landfill for disposal of some types of hazardous spill residuals. The social impact must be considered, however, since the public's image of hazardous materials can be a strong deterent to the disposal of residuals that can be safely placed in a sanitary landfill.

Great caution is needed when sanitary landfills are used in the disposal of hazardous wastes. The action of precipitation (rainfall) has been a major factor in solubilizing hazardous wastes and causing pollutant migration and groundwater contamination.

Sanitary landfills are widely available at reasonable costs. The range of costs for sanitary landfills processing less than 45,000 tonnes/yr(44) is $1 to 6 per tonne (1973 costs). Burial in large size landfills ranges from $0.68 to $1.82 per tonne.

SECURE LANDFILL

Description

In addition to the simple requirements for a sanitary landfill, a secure landfill requires that the site be geologically and hydrologically well-characterized and approved for the disposal of extremely hazardous wastes.(44, 62-64) The site must allow for no discharge of the liquid or solid wastes or their byproducts to ground or surface waters by leaching, percolation, or any other means. Air quality also must not be compromised. Chemical interactions are to be avoided by keeping records of amounts, types, and locations of disposed chemicals. Provisions for leachate monitoring, and collection if necessary, have to be provided for at the secured landfill.

Inputs to the secured landfill site selection process include determination of average rainfall and rainfall patterns in the area and the construction of a site wind rose.(64) Population distribution around the disposal site should be compared with prevailing wind directions. The geological and hydrological field conditions can be obtained from local sources and through a program of drilling. Soil and rock data, as well as information on the depth, occurrence, and quality of groundwater, should be obtained. When impervious basins are desired, suitable artificial or natural liners must be designed; examples include clay layers and plastic liners. The life of the liners should be investigated under the contemplated conditions of use but accelerated life-testing is difficult and controversial. Water-soluble materials of high hazard potential may require asphalt caps, as well as plastic liners. Specific requirements for siting and operating secure landfills have been proposed by the U.S. EPA(5) and have already been established in several states. Capping or covering a filled, secured landfill is essential, as is maintenance of the cover's integrity. Cap cracking, erosion, and gullying readily allow precipitation to enter the fill and enhance backing and migration of stored pollutants.

A secured landfill (e.g., Class I site in California) is a large pit into which any liquid or solid compatible waste may be disposed. One type of secure landfill is illustrated in Figure 10. Examples of hazardous chemicals that can be disposed to a Class I site include aluminium fluoride, antimony pentasulfide, antimony sulfate, antimony trisulfide, nitrochlorobenzene, selenium metal, thallium metal, thallium sulfate, and small amounts of the metal arsenates and arsenites.(44) Many heavy metal hydroxide sludges, resulting from hydroxide treatment of soluble heavy metal salts, also may be disposed to secure landfills.

The requirement to control drainage through the disposal site either limits the location of a secure landfill to arid or semiarid western regions or requires an elaborate system for recovery and treatment of the infiltrate solutions. Though the initial preparation and operating costs are higher for the secured landfill than for the sanitary landfill, the variety of wastes that can be safely disposed is much greater than those in a sanitary landfill. A secure landfill should not, however, be considered as a disposal site for all types of hazardous wastes. For example, California's largest sanitation agency, the County Sanitation District of Los Angeles County, has banned the burial of concentrated cyanide wastes at its Class I landfills in order to prevent dangerous levels of cyanide gas from being created in the working area of these landfills.(65) One must also be concerned with comingling in a secured landfill of wastes that may react violently or produce highly toxic and mobile gases. For instance, the introduction of acids to landfills containing sulfides or cyanides can result in the release of toxic clouds of hydrogen sulfide or hydrogen cyanide.

Proposed RCRA regulations on hazardous waste disposal include requirements for record keeping and reporting (manifest system) and the monitoring of groundwater and leachate from landfills. The location with respect to permanently surveyed bench marks must be recorded for each type of waste disposed in a secure landfill. A groundwater monitoring system consisting of at least four monitoring wells must be maintained. One or more wells must be located in an area hydraulically up-gradient from the landfill and three or more wells located down-gradient. At least one of the latter three must be located immediately adjacent to the active portion of the landfill. Sampling and analysis schedules will be established by State regulatory agencies or the EPA.

Assessment

The disposal of highly toxic hazardous material spill residuals in secure landfills represents an improvement over disposal of these residuals in sanitary landfills. Although chemical destruction, including incineration, is recommended as first priority where possible, it is recognized that landfilling will be less costly or the only alternative available in many incidences involving disposal of spill residuals or releases. Disposal of persistent hazardous substances such as chlorinated hydrocarbon pesticides and toxic heavy metals in a well-designed and engineered secure landfill should provide adequate containment of these materials as long as sufficient control is exercised over operational and

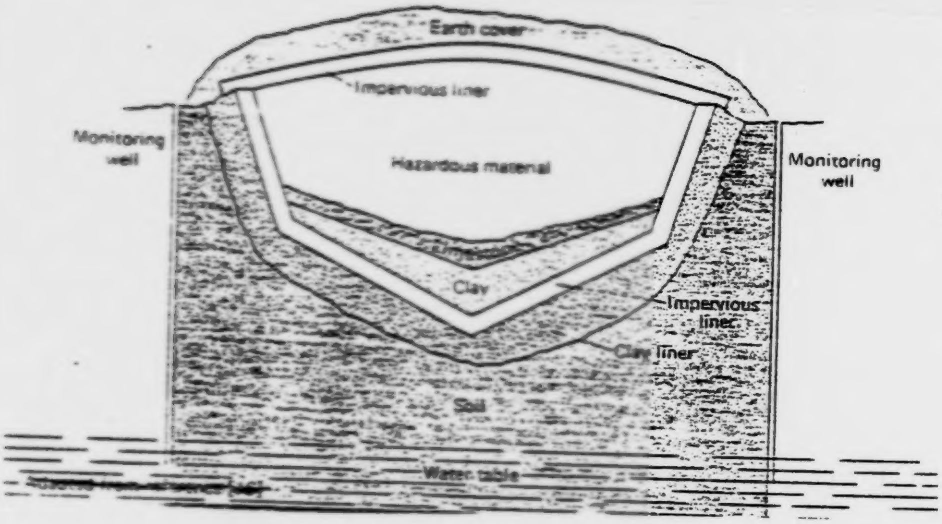


FIGURE 9. Example of a Secure Landfill

retirement procedures. However, questions arise as to the consequences of eventual abandonment of the site and loss of control at some future date. (These problems are addressed in "Superfund" legislation (CERCLA, P.L. 96-510). Would the waste hazardous materials buried in a secure landfill represent severe problems with respect to the health and well-being of future generations? This question has been hotly debated in the case of ultimate disposal of radioactive wastes and many consider it an important question with regard to persistent, highly toxic chemical wastes. Control over a waste burial site cannot be maintained "forever". The burial site markers can be destroyed or removed by acts of vandalism, for example. Records can be lost or destroyed. Climate changes may occur whereby rainfall increases substantially in a formerly arid region. The stability of governments is rarely guaranteed for more than a few hundred years. What happens if--in the distant future--an old, large secure landfill becomes unwittingly exposed to dispersive forces by either natural events or by the actions of man? Any number of scenarios can be written whereby human health and welfare would suffer or devastation of the environment would occur.

The debate over ultimate disposal of radioactive materials has resulted in a more restrictive policy concerning landfilling of radioactive wastes. Only low-level, relatively short half-life radioactive waste is now buried in secure landfills. The U.S. Department of Energy is presently embarked on a major program to convert high-level radioactive wastes to materials, such as glasses, with very low leach rates and to dispose of these materials in geological formations that provide a high degree of confinement. Hazardous, long-lived radionuclides--such as transuranic isotopes--are also designated for disposal at sites where isolation is assured for very long periods of time.

The restrictions that have been applied to the disposal of radioactive wastes could also be applied to those chemical wastes that exhibit a similar degree of hazard. The need to establish such restrictions for chemical wastes has not been demonstrated as this report is being prepared. The EPA Office of Solid Waste Management Programs has suggested that wastes bearing toxic heavy metals, such as arsenic and cadmium, may safely be disposed in a properly designed and operated landfill; ultimately, any decision regarding the environmental adequacy and safety aspects of land disposal of a given waste material must depend on one overall analysis of the individual situation.

A second line of defense against transport of hazardous materials from a secure landfill is warranted for the extremely toxic materials such as soluble arsenic compounds. An effective fixation method--if indeed "effective" can be defined--is a potential approach to assure confinement of these materials in a landfill. Leachate control systems that prevent infiltration of water may also be required to maintain confinement of the waste.

Seven states were reported to have secure landfills in 1977.(66) Additional states such as Oregon have since then joined the list. A map showing the location of these sites is given in Figure 11. The cost of secure landfilling of hazardous wastes can be of the order of ten times that for common sanitary landfilling.

DEEP WELL DISPOSAL

Description

Deep well disposal represents an ultimate disposal system in which waste water is pumped under pressure into deep wells and contained in a permeable subsurface zone that is separated by impermeable rock strata from the surface and subsurface useable aquifers.(67) When the repository zone is dry or contains a noncommercial brine and the waste remains within the desired disposal section, then the technique is a valuable one for ultimate disposal. However, the potential for environmental pollution is high for deep well disposal. Any number of problems may result in the contamination of fresh water aquifers. There is a lack of control of the wastes after they are injected. Because of the expense of drilling several monitoring wells around the injection well the monitoring of waste migration following injection is absent in many cases. Even when unexpected migration of the waste material is detected, there is no easy, low cost way to effectively recover the waste or halt the migration.

To ensure that all of the migration potentials are known, it is generally necessary to undertake a very expensive program of drilling and regional hydrogeologic mapping. In addition, pretreatment facilities may be needed before the waste can be injected. Deep well injection is

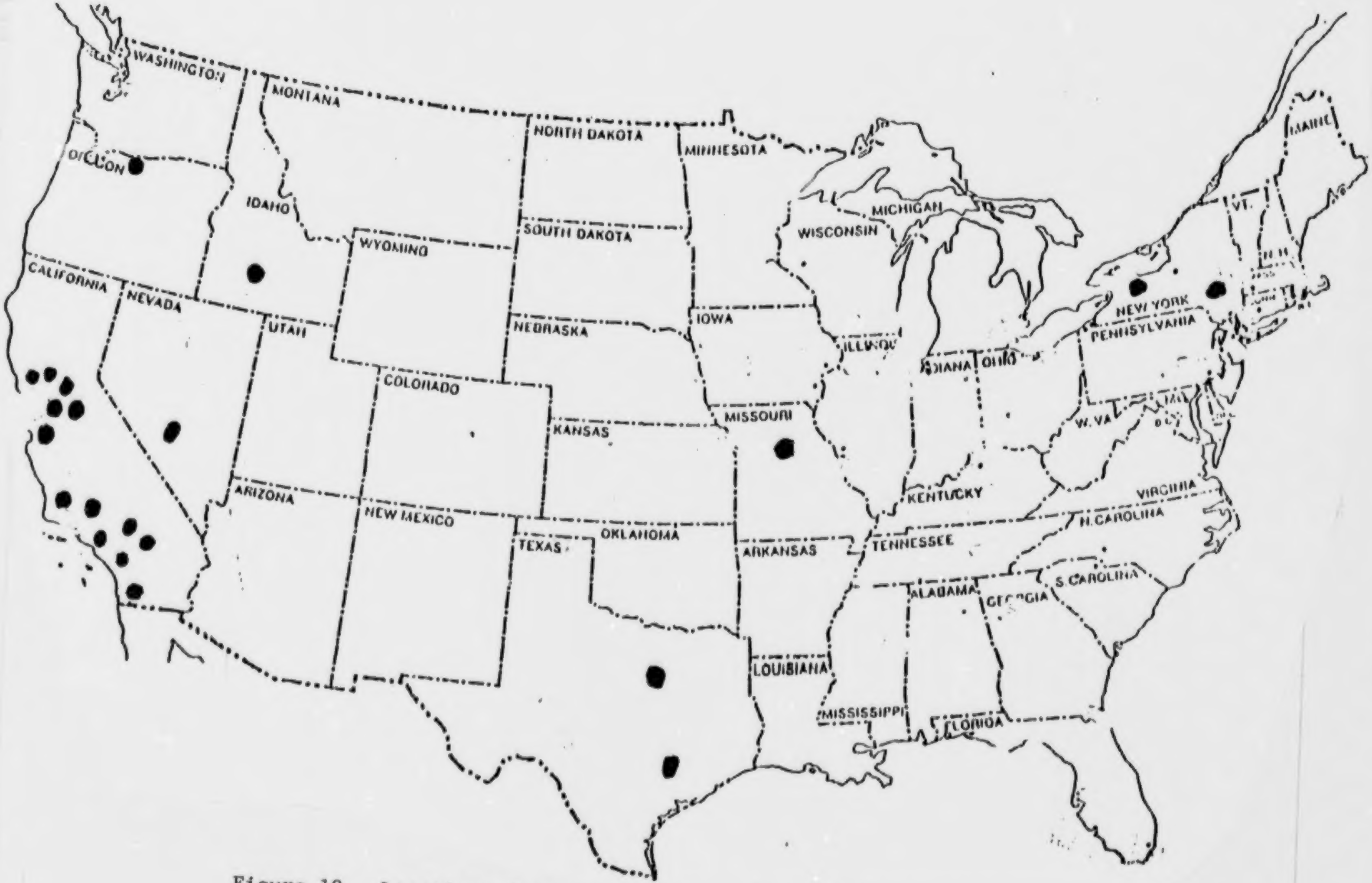

WASHINGTON
OREGON
CALIFORNIA
NEVADA
IDAHO
MONTANA
WYOMING
UTAH
ARIZONA
COLORADO
NEW MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
IOWA
MISSOURI
ARKANSAS
LOUISIANA
WISCONSIN
MICHIGAN
ILLINOIS
INDIANA
OHIO
KENTUCKY
TENNESSEE
MISSISSIPPI
ALABAMA
GEORGIA
FLORIDA
S.CAROLINA
N.CAROLINA
VIRGINIA
W.VA
PENNSYLVANIA
NEW YORK
VT.
N.H.
MAINE

Figure 10. Location of Secure Landfills in the United States

limited to aqueous solutions that are compatible with the geological formations into which the solutions are injected.

The suitability of waste for underground injection depends both on its volume and physical and chemical characteristics and on the physical and chemical properties of the potential injection zones and their interstitial fluids. Wastewater that is suitable for injection must be: 1) low in volume and high in concentration, 2) difficult to treat by surface methods, 3) free of any adverse reaction with the formation fluid or the strata, 4) free of suspended solids, 5) biologically inactive, and 6) noncorrosive.(68,69)

Waste disposal into deep underground aquifers depends on the use of limited storage capacity of the aquifer, and only concentrated, very objectionable, relatively untreatable wastes should be considered for injection. The fluids injected into deep aquifers do not occupy empty pores as in the vadose (surface) zone, but displace the fluids that saturate the storage zone. Consequently, optimal use of the underground storage space will be realized by the use of underground injection only when more satisfactory alternative methods of waste treatment and disposal are not available.

Reaction of the wastewater with the formation water or the strata must be considered. Resulting problems include dissolving the formation, generating a gas or precipitate in the formation, and clogging by biological growths. Walker and Stewart(70) suggest a laboratory test to ensure compatibility of the wastewater with the formation. The wastewater is mixed in a beaker with a formation water sample and held at formation temperature to see whether there is any precipitate or adverse reaction. Pumping the wastewater through a core sample can reveal possible clogging problems. The wastewater should be free of suspended solids and biologically inactive to avoid reservoir clogging. The corrosiveness of the wastewater should be low to prevent tubing and pump corrosion.

Assessment

Deep well injection is a viable option for the disposal of aqueous solutions of certain types of hazardous materials; however, there are presently only 6 injection wells identified in the United States that can handle hazardous wastes and three of them are located in Texas.(66) The lack of available injection sites coupled with the low probability of encountering aqueous solutions that are acceptable for deep well injection is expected to result in little use for this method of ultimate disposal for hazardous material spill residuals. Concentrated brines from residue treatment processes may be an exception. Some claim that disposal of these solutions into existing brine aquifers can bypass expensive evaporation processes without creating adverse impacts, but the subject is controversial.

OCEAN DISPOSAL

Description

The oceans have long been used by man as ultimate refuse disposal areas, and have come into much greater use for waste disposal with the advent of industrialization. Many of our most hazardous wastes, such as munitions and other martial tools, have been disposed by scuttling obsolete munitions-loaded ships at sea. Various sludges and liquid wastes are barged to sea and dumped. The liquid and solid wastes may be very acidic or basic because the sea acts as both a diluent and a system pH buffer allowing disposal of acids, bases and toxic materials. Incineration of chlorinated hydrocarbons has been undertaken at sea in special incinerator ships to take advantage of the buffering capacity of the ocean without having to resort to caustic scrubbing of HCl and to minimize the ecological effects. The ocean dumping of radioactive wastes has been severely curtailed. Improved packaging is required and the dumping of high level radioactive waste is prohibited.

Certain areas of the Atlantic and Pacific Oceans and the Gulf of Mexico have been designated as ocean dumping areas. However, with the renewed interest in offshore oil drilling and manganese module recovery from deeper ocean areas, the waste disposal and mining or drilling areas of interest may begin to overlap. Consequently, a permit system was initiated by the Environmental Protection Agency.(71) There are several permit categories for waste disposal including general, special, emergency, interim, and research permits. General permits authorize dumping of nontoxic wastes in small quantities. Special permits are valid for three years and allow dumping of materials not covered by the general permit except toxic metals, oils, inorganic wastes, and BOD producing materials. Emergency permits allow dumping of prohibited materials when there is no other alternative disposal procedure due to emergency conditions. Interim permits are used during development and execution of other acceptable waste disposal plans. Research permits are granted when the benefits of a project outweigh the potential environmental hazards of ocean disposal of its waste products. The EPA will not allow dumping of high level radioactive wastes, biological or other warfare agents, and unknown materials or materials that persist in suspension. Stringent requirements are maintained on dumping of organohalogens, cadmium, mercury, and oils. Current restrictions are now supported by international convention and are the subject of further discussion and probable tightening.

Assessment

Restrictions placed on ocean dumping of water have substantially reduced the number of materials that can be disposed via this route. Furthermore, only a few contractors located in six states across the country have facilities available for ocean dumping. Although ocean dumping is a viable option for some hazardous material residuals, the lack of available facilities and regulatory restraints limit the use of this method of ultimate disposal.

APPLICATION OF CONVENTIONAL DISPOSAL TECHNOLOGY

Spill Characteristics

Hazardous material spills and releases can occur under a wide variety of conditions on land as well as in water and may involve small or large quantities of material that range from essentially nontoxic to deadly. Depending on the circumstances, spillage of a hazardous material may or may not result in the formation of a hazardous waste requiring disposal by methods set forth under RCRA. A moderate or small spill of highly volatile material, e.g., liquefied petroleum gas (LPG), will usually evaporate and disperse to the atmosphere leaving little or no residue. A spill of soluble material in a large rapidly flowing stream may be so quickly diluted and dispersed that nothing can be recovered for disposal. In many cases, especially for spills on land, the release or spill residue may not be considered hazardous and disposal to a sanitary landfill or municipal sewage treatment plant would be permitted. Common, low-toxicity materials such as methanol, ethanol, acetone and other readily biodegradable organics (corn syrup) can be disposed at a municipal sewage treatment plant or, in some instances, simply allowed to drain into soil where natural biological degradation will take place. Hazardous materials mixed with soil will frequently be rendered nonhazardous because of neutralization or fixation by the soil. Spilled strong acids such as sulfuric or hydrochloric that percolate into soil will generally be neutralized by the soil. Ammonia spilled in water is toxic to fish but ammonia spilled on land may be readily sorbed by soil and not create much of a problem. Designation of a spill residue as hazardous will depend on criteria and tests to be established by regulatory agencies. Proposed criteria can be found in the Federal Register, Volume 43, No. 243 - Monday, December 18, 1978.

Admixture of spilled hazardous material with extraneous matter will frequently dictate the type of disposal method to be used. Four basic types of mixtures were considered in determining the type of disposal needed:

- Mixtures with minor amounts of extraneous matter,
- Mixtures with or solutions in water,
- Mixtures with combustible material,
- Mixtures with noncombustible material.

Recovery and reuse of spilled hazardous material should be undertaken whenever possible. In many instances, mixtures with minor amounts of extraneous matter may be processed for recovery of the spilled material. Recovery of spilled oil is often practiced since extraneous matter mixed in oil can frequently be separated without much difficulty. When recovery is not practical, disposal of spill residuals mixed with minor amounts of extraneous matter can generally be accomplished in a manner similar to that recommended for the pure material.

Mixtures or solutions in water constitute a separate category because processes such as gravity sedimentation, absorption, ion exchange or precipitation are frequently used to remove the spilled hazardous material from the water. In some instances (e.g., caustic spills), the spilled hazardous material may be disposed by neutralization in the aqueous solution. Materials removed from water are subject to appropriate disposal methods.

Mixtures of spilled hazardous materials with combustible matter are placed in a separate category from those with noncombustible matter since incineration is a viable option when the mixture is combustible and degrades to suitable end products. In case of mixtures between categories (e.g., a spill mixed with both combustible and noncombustible matter), judgment is necessary in selecting an appropriate disposal method. For example, a sizeable fraction of noncombustible matter in a large quantity of spill mixture may render the whole mixture unsuitable for incineration. Mixtures of water with insoluble combustible or noncombustible matter may be either settled, screened, or filtered to remove the water.

Method Evaluation Matrix

A matrix was prepared to aid in evaluating conventional disposal technology for spilled hazardous materials. The initial approach to preparing such a matrix included classification into families for chemical compounds that possessed the same or similar chemical and physical characteristics. Disposal methods were to be selected and evaluated for each of these separate classifications. This approach was abandoned, however, because the number of classifications was too large and did not adequately focus attention on problems associated with disposal of highly hazardous, persistent materials.

An alternate approach was adopted whereby spilled hazardous wastes are divided into two categories, organic and inorganic. The organic materials are subdivided into reactive, unreactive, and highly-toxic persistent whereas inorganic materials are subdivided into reactive and highly-toxic persistent. The evaluation matrix presented in Table 3 utilizes these five categories of hazardous materials combined with the four basic mixtures with extraneous matter discussed in the previous section. Only materials designated as hazardous waste under proposed RCRA regulations are included in these categories. Spill residues that are nonhazardous may be disposed of by conventional methods such as sanitary landfills or municipal solid waste incinerators.

The subcategories "reactive" and "unreactive" pertain to the ease with which the materials can be biochemically or chemically treated to form less hazardous or nonhazardous materials. Reactive materials can be treated in situ at the spill site or recovered and treated by methods presented in the User's Manual for the Control and Treatment of Hazardous Material Spills.(45) Treatment, designated by the letter "B" in the matrix, includes biochemical and chemical methods that may either occur naturally or be induced by personnel responding to the spill. Unreactive materials cannot be readily altered to less hazardous or nonhazardous forms by simple aqueous chemical or biochemical methods and are either incinerated (designated by letter "O" matrix) or disposed to a secure landfill (designated by letter "S" in matrix). Diluted materials in aqueous solution may be concentrated by chemical or physical methods.

TABLE 3. MATRIX FOR CONVENTIONAL DISPOSAL METHODS

Composition	Hazardous Organic Waste			Hazardous Inorganic Waste	
	Reactive	Unreactive	Highly Toxic/ Persistent*	Reactive	Highly Toxic/ Persistent*
Mixture with minor amounts of extraneous matter	B O S	O S	O S	B	F-S
Mixture with substantial amount of water	A-B A-O A-S	A-O A-S	A-O A-S	B	A-F-S
Mixtures with combustible solids	B O	O S	O S	B	F-S
Mixtures with small non-combustible solids	B S	S	S	B	F-S

B = Treatment (biochemical or chemical)
O = Incinerate
S = Secured landfill
F = Fixation
A = Concentrate and remove from water
* = See Appendix A for listing

(designated by letter "C" in matrix) to cleanup the water and reduce the residue to a small volume for disposal. The method used to concentrate the hazardous material may also render the material nonhazardous. Adsorption of the material on activated carbon, for example, may fix the material so that it is no longer leachable at hazardous levels. As previously discussed, precipitation can be used to remove and concentrate hazardous materials for disposal but the precipitate may or may not qualify as a hazardous material, depending on the solubility of the precipitate and the toxicity of the hazardous constituent contained in the precipitate. Disposal methods are listed from top to bottom in order of preference.

The highly toxic, persistent subcategory includes organic materials that are unreactive and persist in the environment beyond one year and represent an especially great hazard due to unacceptable levels above 1 mg/L in water. This category of organic hazardous materials includes a number of pesticides that represent a substantial threat to the environment when not properly disposed. Inorganic highly-toxic, persistent materials are limited to substances containing sufficient leachable arsenic, barium, cadmium, chromium, mercury, lead, selenium, or silver to qualify as hazardous. The list of hazardous materials in Appendix A also includes information concerning amenability to biological or chemical treatment or incineration and designates those materials in the highly-toxic, persistent category and those defined as hazardous or potentially hazardous under proposed RCRA regulations.

Chemical treatment indicated in the matrix presented in Table 3 is limited to: 1) neutralization with acids and bases, 2) oxidation and reduction at atmospheric pressure with common oxidants and reductants such as hypochlorite and sulfite, and 3) precipitation. Chemical or physical fixation is included only for inorganic material since this method is not considered to be a conventional technique for organic material. Ocean disposal and deep-well injections are not included because of anticipated restrictions on these disposal methods.

A discussion of the matrix in Table 3 is provided in the following subsections for each of the subcategories of hazardous materials as applied to the four basic mixtures.

Organic-Reactive. This subcategory includes many materials that can be decomposed to innocuous end products by biological or chemical treatment methods. Reference to the User's Manual for Control and Treatment of Hazardous Spills(43) is recommended to determine the type of treatment for a particular material. Materials not listed in the User's Manual including industrial process or waste mixtures will require judgment on the part of the On Scene Coordinator (OSC) to select the proper method. Similarity to materials listed in the manual can be used as a guide in selecting a specific method or methods. Consultation with experts in the field can hardly be overemphasized to assure selection of appropriate methods.

Hazardous wastes that can be readily biodegraded include aliphatic acids, acetone cyanohydrin, phenol, formaldehyde and many others listed in Appendix A. Dilution and neutralization of the spill residue may be accomplished by one or more of several different methods. The organic substances listed above that biodegrade readily can usually be discharged to a biological treatment plant under controlled conditions to avoid overloading the plant. Alternately, in situ biodegradation is frequently possible by allowing the material to remain in the soil into which it drains from a spill site. This approach is possible where there is no threat to ground or surface waters or to personnel in the vicinity of the spill. Chemical methods should be given priority where possible for reactive materials that are highly toxic to quickly ameliorate the effects of the spill. Incineration is considered applicable to all hazardous organic materials except organometallic substances such as tetraethyl lead. Although incineration has not been evaluated for all the organic compounds listed in Appendix A, it is assumed that, with proper temperature control and residence times in the incinerator coupled with suitable scrubber/filter systems, incineration represents a viable disposal alternative for these materials.

The availability and cost of operating incinerators are the principal limitations to widespread use of this method for disposal of spilled hazardous materials. As a consequence, chemical or biological treatment is given preference over incineration for the Organic-Reactive group of materials.

Disposal in a secure landfill is the third option that can be used although priority is given to the first two options, treatment and incineration, which destroy and eliminate the spilled material. However, in this subcategory there are a number of materials that will anaerobically or chemically degrade in the landfill and would not present long-term problems. Alcohols, aldehydes, ketones, carboxylic acids, and carbohydrates are examples of materials that undergo relatively rapid anaerobic decomposition. (Petroleum-based oils are not good candidates for anaerobic decomposition although landfilling is a common disposal method for these materials. Landspreading for the more rapid aerobic decomposition process is the preferred method. Waste oils are designated as hazardous.)

A discussion of disposal options for each of the basic types of mixtures under reactive organic hazardous waste is presented below:

1. Mixtures with minor amounts of extraneous matter. Methods outlined in the User's Manual(43) are appropriate for most of the materials in this group insofar as treatment by disposal is concerned. Treatment is generally the preferred option followed by incineration and then secured landfilling. Contaminated petroleum-based oils, which represent a large fraction of the total spills, would in the majority of cases be recovered rather than disposed when containing only minor amounts of extraneous matter. Oils not recovered follow the priority of: 1) treatment by land spreading, 2) incineration,

and 3) landfilling. In order to reduce the mobility of the oil for landfilling, the oil should be absorbed in some porous material prior to disposal. Whether oils mixed with absorbent materials constitute a hazardous waste in all cases is uncertain. Regulated quantities of oily material may be disposed in sanitary landfills rather than in secured landfills.

2. Mixtures with water. Methods outlined in the User's Manual for Control and Treatment of Hazardous Spills will be appropriate for most of the materials in this group since the methods assume the presence or use of water. No further action is required when treatment renders the material nonhazardous in the water (e.g., neutralization of acids and bases). However, many of the materials may be removed from the water by sorption methods and the sorbent containing the spill residue will require disposal. Hazardous materials sorbed, precipitated, or ion exchanged from water may be disposed by chemical or biological treatment, incineration, or secured landfilling. An oxalic acid solution, for example, may be neutralized with lime to precipitate calcium oxalate, which can be biologically degraded, incinerated, or landfilled. Activated carbon adsorption is commonly used to remove organic materials that have limited solubility in water. Very soluble substances cannot be readily adsorbed by activated carbon but will undergo rapid biological degradation when sufficiently diluted in water. Dilution with water may also render the material nonhazardous. Oil-water emulsions are preferably treated by land spreading although incineration is possible (e.g., but supplemental fuel may be required) and landfilling may be permitted when the waste is mixed with sorbent material.

3. Mixtures with combustible solids. All three disposal options may be used with these mixtures. The choice depends on: the nature and toxicity of the spill residue, the availability of facilities or equipment, and the characteristics of the combustible solids. Large objects (e.g., wooden items) contaminated with soluble, low-toxicity, reactive organic spill residues may be rinsed with water with the rinse water then being routed to a biological treatment facility or spread on land (if suitable acreage is available). Small objects (e.g., grass, sawdust) contaminated with these same substances may be treated by land spreading (if volatility is not a problem) or placed under water in a biological treatment lagoon. Water-insoluble materials such as oily wastes can be disposed by land spreading even when the waste is mixed with small objects. Large objects are best removed.

4. Mixtures with noncombustible solids. The presence of substantial amounts of noncombustible solids normally rules out incineration as an economic treatment option. The utility of chemical or biochemical treatment and secure landfill disposal are essentially the same as in 3.(above).

Unreactive Organic Hazardous Wastes. These materials cannot be chemically or biochemically treated by conventional methods; therefore, disposal is normally limited to incineration or secured landfilling. Since the hazardous constituents of these wastes are persistent, incineration is much preferred over secured landfilling . Disposal of mixtures in this category by incineration and secured landfilling will be similar to that in the "reactive organic" category except dissolution in water will generally be more difficult.

High-Hazard Persistent Organic Waste. Disposal is also limited with little opportunity for chemical and biochemical treatment and even more emphasis is placed on incineration as the preferred disposal method. Secured landfilling is not considered to be an acceptable long-term disposal method for these substances; however, it should be is recognized that mixtures of these substances with extraneous matter complicates alternate disposal methods. Further research and development is needed in this area to establish suitable alternatives to landfilling.

Hazardous Reactive Inorganic Wastes. For these wastes, the use of incineration as a disposal method is excluded but fixation processes may be useful especially where fixation can be demonstrated to produce a material that is stable for an indefinite time period under conditions present or anticipated at the disposal site. A discussion of the disposal of each type of mixture is presented below:

1. Mixtures with minor amounts of extraneous matter. Treatment to destroy the hazardous substance is the preferred option in this subcategory. Neutralization of strong acids and alkalis are common examples of this type of treatment. Residuals following such treatment are usually nonhazardous. When hazardous residuals are produced, further treatment is required. Oxidation of cyanide is included as a disposal method in this subcategory.

   Disposal of reactive substances such as antimony pentachloride requires special attention since the hazards are associated with the violent reactions expected and the toxic gases (e.g., HCl) that may be evolved.

2. Mixtures with water. Treatment is similar to (1) above except substances that react with water need not be dealt with unless a hazardous residual (such as HCl) remains.

3. Mixtures with combustible solids. Treatment and disposal may require rinsing with water to remove the hazardous substance for transfer to a vessel for better control of the chemical reaction. Oxidation of cyanide may be inhibited by the presence of combustible matter, which may be oxidized preferentially. Neutralization of acids and alkalis may be accomplished in a mixture when good mixing or contact with the neutralizing agent can be achieved and excessive heat release controlled.

4. Mixtures with noncombustible solids. Treatment and disposal is similar to (3) above; however, noncombustible solids such as sand are more inert and may not interfere with the reaction. Soil is

considered noncombustible but may contain material that would interfere with or participate in oxidation/reduction reactions.

High-hazard Persistent Wastes. These wastes contain the hazardous heavy metals (As, Ba, Cd, Hg, Pb, Se, Ag). Low-temperature fixation and secured landfilling are the disposal methods commonly employed. Low-temperature fixation methods may not achieve the very low leach rates needed for safe, long-term storage; therefore, further research and development is recommended to establish superior waste forms for disposal. The presence of organic matter may inhibit fixation. Effective separation techniques are also needed to remove these metals ions or complexes from extraneous matter.

SECTION 6

THE HAZARDOUS WASTE PROCESSING INDUSTRY

Previous segments of this report have been dedicated to a discussion of technological options for disposing of hazardous wastes. Little, however, has been directed to suggest who should execute those processes. There is, in fact, a hazardous waste industry that specializes in doing just that. In a recent review of the industry, Lehman(72) reported that, in 1975, there were 95 firms operating 110 sites in the United States. Some 57% of these firms are privately owned while the remainder are publicly held, either directly or through parent corporations. Only 8% of the firms are municipally owned; they are in California. Employment in the waste processing industry is estimated at 2,000, 11% of which positions are classified as professional. The capacity of the industry was judged to be 6.6 million tonnes per year in 1975; however, only 73% of that capacity may be deemed environmentally acceptable as disposal regulations come on-line. It is further estimated that only 53% of that capacity is presently being utilized. Hence, the industry can readily accept residuals from spill clean-up activities at this time. This situation may reverse itself with promulgation of proposed RCRA regulations. Projected volumes of regulated hazardous wastes will exceed current capacity.

There are compelling reasons why the hazardous waste industry should be employed as the first alternative for disposal of spill residuals:

1. The operators are experienced in the handling, treatment, and disposal of these materials and can therefore minimize the risk of improper management;

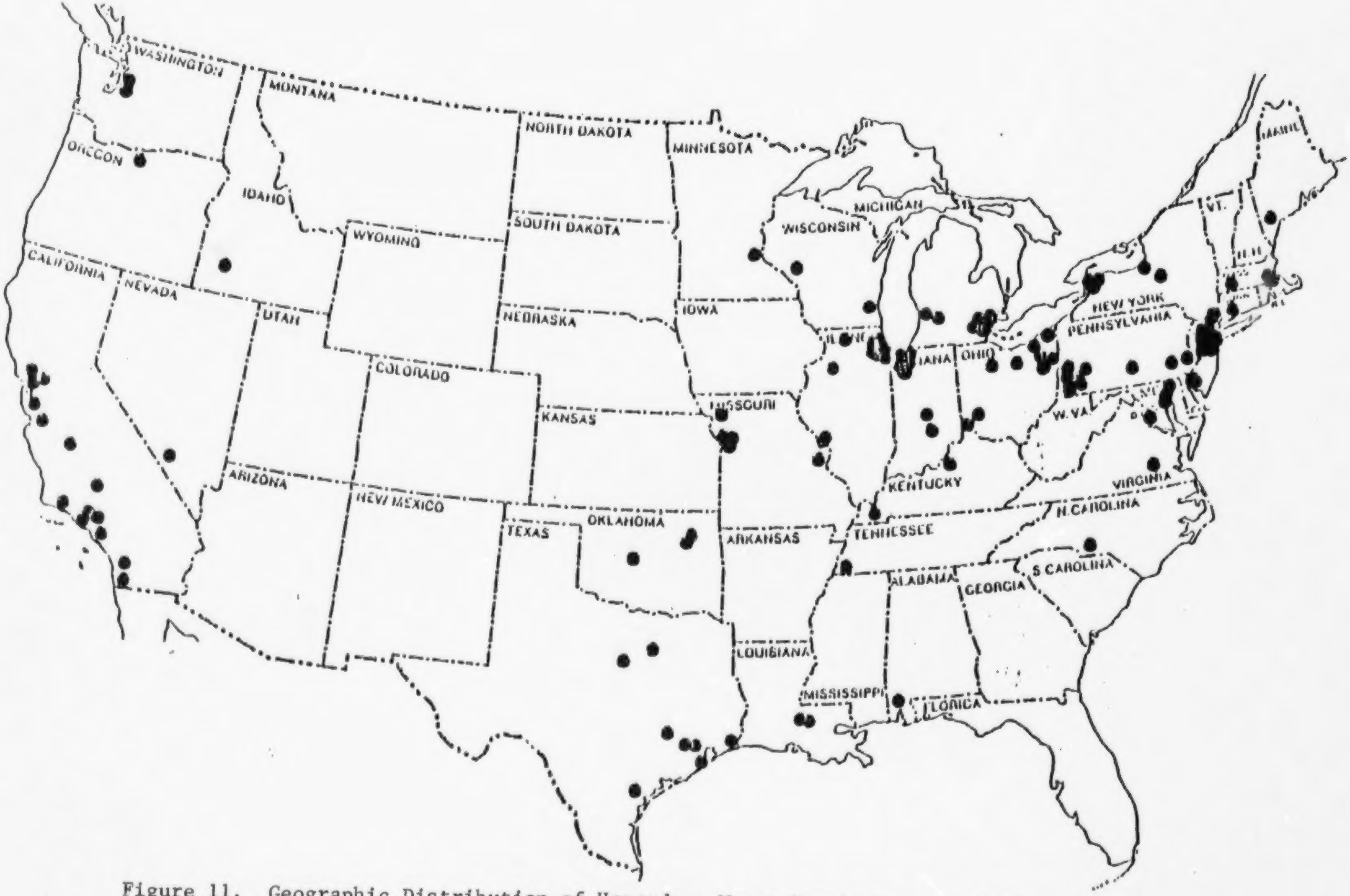
2. The organizations have the facilities and equipment available to perform the necessary processes in an expeditious manner; and

3. Regulations to be promulgated under the Resource Conservation and Recovery Act will soon require that disposal of hazardous wastes be conducted only at permitted facilities found to meet specific standards.

The U.S. EPA's, Office of Solid Waste Management Programs issues a periodic index of "Hazardous Waste Management Facilities in the United States." This pamphlet gives a brief synopsis of the capabilities of operating firms and describes the kinds of wastes that they can accept. Facilities identified in 1977 are located on the map in Figure 11.

It must be noted that while the hazardous waste industry should be the first choice for management of spill residuals, it will not always be the best option. Use of existing facilities will often require transporting spill residues great distances. This raises further risk of spillage and exposure. Transport may be impractical or impossible if any of the intermediate states that must be crossed refuse passage. Finally, the state in which the facility of choice is located must permit use of that facility for the spill residuals. These problems are minimized when an acceptable site is operating within the state where the spill or release occurs. Complications magnify with the distance between the spill and the disposal facility. As is evident from Figure 11, the greatest difficulties can be expected in the Rocky Mountain, Midwest and Southern States.

Regardless of the latter considerations, the use of the hazardous waste industry for spill residuals disposal is recommended whenever possible. Upon characterization of wastes from clean-up activities and confirmation that they are hazardous, the EPA index should be consulted to determine the nearest firms capable of handling these wastes. Contact should then be made to ascertain the feasibility of using that site. Many times the operator can provide properly equipped and placarded vehicles for transportation to the site as well.


WASHINGTON
OREGON
CALIFORNIA
NEVADA
IDAHO
MONTANA
WYOMING
UTAH
ARIZONA
COLORADO
NEW MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
IOWA
MISSOURI
ARKANSAS
LOUISIANA
WISCONSIN
MICHIGAN
ILLINOIS
INDIANA
OHIO
KENTUCKY
TENNESSEE
MISSISSIPPI
ALABAMA
GEORGIA
FLORIDA
S CAROLINA
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VIRGINIA
W. VA.
PENNSYLVANIA
NEW YORK
VT.
N.H.
MAINE

Figure 11. Geographic Distribution of Hazardous Waste Management Facilities

SECTION 7

NOVEL DISPOSAL METHODS

Novel disposal methods, which are in various stages of development, were investigated to determine their potential for ultimate disposal of spilled hazardous materials. Emphasis was placed on disposal methods for extremely hazardous and persistant materials.

THERMAL DESTRUCTION

Cement Kilns

Recent work on the destruction of PCB's in cement kilns(73) shows promise of providing an alternate incineration method that would be much more widely available than the waste incinerators currently designed for this purpose. Normal operation of cement kilns is in the range of 1370 to 1450°C with a very long gas residence of more than 10 seconds, more than adequate for decomposition of most chlorinated hydrocarbons. The alkaline substances in the raw material fed to these kilns act as efficient scrubbers for the HCl produced.

Two cement kilns in New York State have been successfully used for short periods of time to incinerate chlorinated organics and other chemical process wastes.(41) In both cases, the plants benefited from the reduction of the alkali content of their cement product and from the heating value of the wastes. However both the cement firms involved have discontinued burning the chemical wastes because a reliable supply of this material was not available. A continuous, reliable supply is needed to justify the added costs for the liquid injection systems.

Nearly one year of successful operation was also conducted at the St. Lawrence Cement Co. in Mississauga, Ontario. Further investigations of this technology are currently underway in an EPA sponsored study.

Institutional barriers (public outcry) severely limit the use of cement kilns for hazardous waste disposal; most kilns are not sited in areas of low population density.

Molten Salt Incineration

Molten salt incineration is a relatively new combustion technique involving dispersion of the gaseous or liquid waste in a molten, high temperature salt. Eutectic mixtures of NaOH-KOH or Li_2CO_3-Na_2CO_3-K_2CO_3, have been suggested(30) (Yosim, et al.,1973) for molten salt baths in which unwanted explosives and propellants are burned. Another design(31) (Yosim, et al 1974) suggested the use of a sodium carbonate-sodium sulfate molten bath to destroy organic pesticides at 900 to 950°C. The reaction becomes exothermic when the pesticide reacts with oxygen in the air that is forced through the salt bath. Enough heat is generated to keep the salt bath molten. Since molten salt incineration has had very limited use in practical applications, more experience is required before it can be properly evaluated for use with hazardous wastes.

Atomics International proposed that hazardous wastes, particularly pesticide wastes including used pesticide containers, be combusted in a molten salt furnace. Using a melt consisting of 90% sodium carbonate and 10% sodium sulfate and operating temperatures of 800 to 1000°C, 99.99% destruction of DDT, 99.96% destruction of chlordane, and 99.98% destruction of 2,4-D were obtained in a test reactor. No hydrogen chloride or organic chloride could be found in the melt or the exhaust gases as the halogens reacted with the salt to form sodium halides. Phosphorus, sulfur, arsenic, and silicon form their respective oxygenated sodium salts. This conversion to salts that remain in the melt eliminates the need for scrubbing required with other types of incineration.(40)

CHEMICAL DESTRUCTION

Bromination Process

The Atomics International bromination process is currently being investigated for the disposal of organic spill residues.(74) Organic materials are first reacted at a moderate temperature of about 300 C with bromine and water to produce carbon dioxide and hydrobromic acid according to the following equation:

$$CH + 2H_2O + 5/2\ Br_2 \longrightarrow 5HBr \text{ (aqueous solution)} + CO_2.$$

Off-gas from the reaction is stripped of HBr and excess Br_2 and the CO_2 is released to the atmosphere. Bromine is recovered from the HBr by electrolysis by the following reaction:

$$5\ HBr \text{ (aq. soln.)} \longrightarrow 5/2\ H_2 + 5/2\ Br_2 \text{ (in dil. HBr soln.)}$$

The bromine is returned for further reaction and the H_2 is stripped of Br_2 and HBr vapors prior to disposal or reuse. A schematic flowsheet for the process is presented in Figure 12.

Oxidation of materials such as copper acetate, malathion, and trichloroethane were achieved on a laboratory scale at temperatures of 300°C and reaction times of one, three and five hours respectively. Copper bromide produced by bromination of copper acetate can be recovered as copper sulfate for reuse by reactions of sulfuric acid. Reaction with sulfuric acid evolves HBr, which is recycled. Oxidation of malathion forms sulfuric and phosphoric acid, which can be precipitated from the electrolysis liquor with lime.

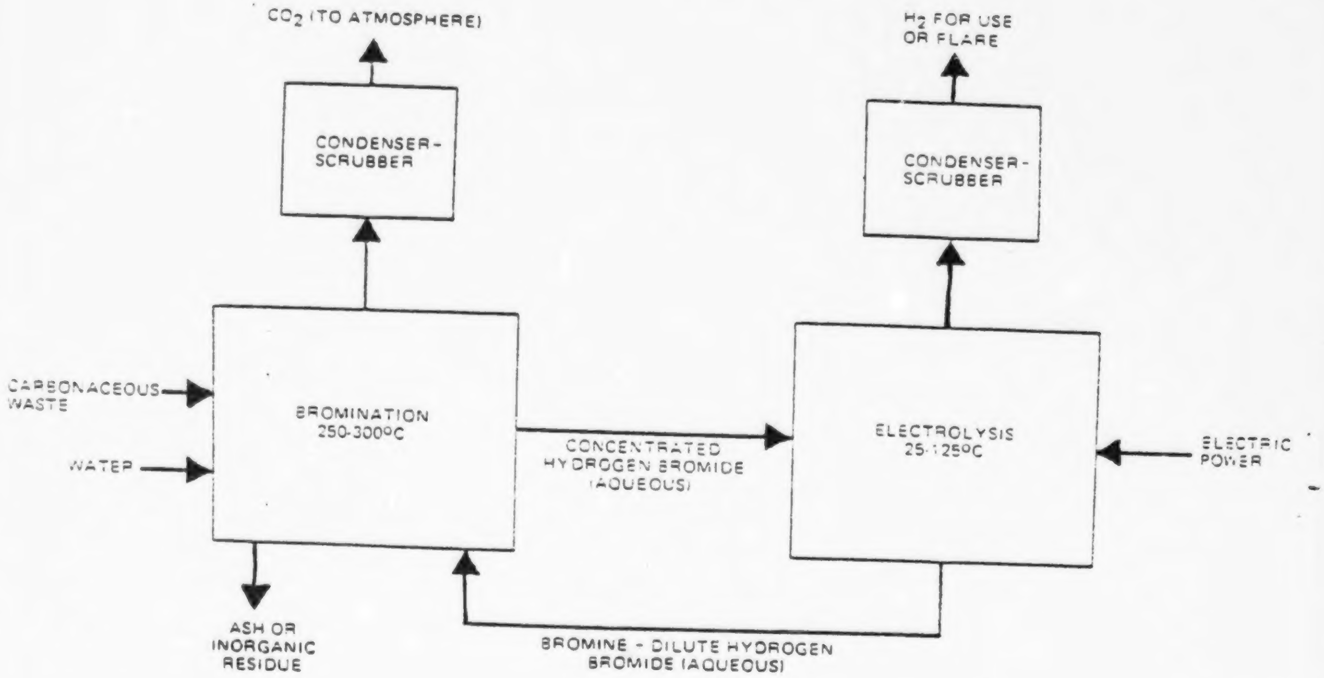
CO_2 (TO ATMOSPHERE)
CONDENSER-SCRUBBER
H_2 FOR USE OR FLARE
CONDENSER-SCRUBBER
CARBONACEOUS WASTE
WATER
BROMINATION 250-300°C
CONCENTRATED HYDROGEN BROMIDE (AQUEOUS)
ELECTROLYSIS 25-125°C
ELECTRIC POWER
ASH OR INORGANIC RESIDUE
BROMINE - DILUTE HYDROGEN BROMIDE (AQUEOUS)

Figure 12. Flowsheet for Bromination Process for Destruction of Hazardous Organic Materials

Sodium Reduction Process

A sodium reduction process was being developed under contract by the EPA for the destruction of halogenated organic materials and other substances that undergo reduction reactions with elemental sodium to produce nonhazardous end products. Elemental sodium reacts with chlorinated hydrocarbons, for example, to produce sodium chloride, carbon (graphitic) and hydrogen. The liquid sodium metal system is designed along the lines of current heat transfer equipment and uses technology derived from inert gas cleaning equipment. The carbon is filtered from the molten sodium and collects in a "cold trap" along with inorganic salts. The hydrogen is flared. Destruction is complete to limits of detection of waste (2-chloro-4-phenyl phenol, Kepone, sodium fluorosilicate, antimony trisulfide).

BIOCHEMICAL DESTRUCTION

The feasibility of using selected pure cultures of microorganisms is under investigation for use in degrading spilled hazardous material residuals.(75) Certain organisms are known to be effective for metabolizing normally biorefractory substances; however, practical use of such organisms depends on their ability to survive in the presence of indigenous bacteria. Pentachlorophenol, hexachloropentadiene, and methyl parathion were successfully degraded in laboratory screening tests. Greater than 90% removal of pentachlorophenol was achieved in a continuous pilot scale unit operated at 2 liters per hour with a residence time of 48 hours and populated either with a bacterium or a fungus. Through control of operating parameters, growth of indigenous bacteria that may consume contaminant-degrading species is minimized.

MICROWAVE DECOMPOSITON

A microwave decomposition process for the decomposition of organic wastes and pesticides has been reported by the Lockheed Palo Alto Laboratories and the Solid and Hazardous Waste Research Division of the U.S. EPA in Cincinnati, Ohio.(76) The microwave system consists of a reactor through which the waste passes. Microwaves energy is applied to the reactor and forms a plasma or ionized gas that breaks down the waste by ion and electron impost reactions. Recovery of byproducts was emphasized in the work. For example, phenylmecuric acetate was decomposed to water plus carbon dioxide and carbon monoxide, with the mercury recovered in the metallic form. Methyl bromide and polychlorobiphenyls have also been decomposed in the same system. The process handles a kilogram per hour presently but may be scaled up to about 50 kg/hour.

Wet-air oxidation of hazardous organic materials is another possible process for rendering these substances in nonhazardous forms. This process is being investigated for treatment of hazardous industrial wastes through the Hazardous Waste Research Division of the EPA in Cincinnati, Ohio.

ADVANCED FIXATION METHODS

The disposal of toxic heavy metals such as cadmium and arsenic can present long-term storage problems. These toxic substances--being elements--cannot be chemically decomposed; alternative processes such as fixation in a form that exhibits very low leachability must be used. Incorporation of these substances in a suitable glass is one possibility currently being explored by the EPA. Borosilicate glass is one of the leading candidate processes for fixation of high level radioactive wastes. Glass has the advantage of being a very inclusive material and many elements of the periodic table can be incorporated in glass as network formers or modifiers even though these elements are not glass formers by themselves. A typical borosilicate glass used for high level waste fixation will contain 20 to 35% of waste oxides and the leach rate will be in the range of 10^{-4} to 10^{-7}g/cm^2 per day. Soluble constituents such as cesium will exhibit a high leach rate whereas insoluble constituents such as cerium may have a leach rate that is 2 to 3 orders of magnitude less.(78) The leach rate of a high quality glass will generally be several orders of magnitude less than that of a low temperature fixation product such as an asphalt mix.

One problem with glassification methods is to ensure that the hazardous waste is uniformly dispersed as very fine particles throughout the glassy matrix. In an effort to reduce clumping of the waste, a mixture of finely powdered glass and inorganic waste was thoroughly mixed with a "Thermite"-like material and the resulting powder was compacted into a billet. Upon ignition, the mass fused into a dense frit that had very low leachability characteristics. Unfortunately, the hot billet released some hazardous inorganics as vapors during melting, an aspect that is undesirable since a chamber must be placed around the billet during fusion and then the enclosure must be subsequently cleaned.(75A)

APPLICATION OF NOVEL DISPOSAL TECHNIQUES

Need for New Disposal Methods

Evaluation of conventional disposal methods for spilled hazardous material residuals has revealed the need for additional methods to fill the gap where conventional methods are either inadequate, uneconomical, or frequently unavailable. One such gap involves destruction of chlorinated hydrocarbons. The availability of a suitable incinerator for particularly persistant and hazardous materials such as PCB's can be a problem in many areas of the United States. Of particular concern is the disposal of small quantities of highly toxic persistant materials.

The disposal of mixtures of hazardous spill residuals with extraneous matter represents another of the major problems with respect to extremely toxic and persistant substances. Conventional disposal methods may not be readily adapted to these materials. Disposal in a secure landfill does not provide adequate long-term protection for the highly toxic peristant materials. Therefore, efforts should be focused on substituting other methods that do provide the protection desired. The EPA is currently considering various techniques for extracting or leaching the spill residuals from mixtures with extraneous matter (such as soil or sediments) in order to more readily convert the residuals to forms more suitable for ultimate disposal.

Modified Evaluation Matrix

An evaluation matrix incorporating novel disposal methods was prepared to determine the potential for achieving adequate environmental protection with the use of these methods. The basic change included in the modified matrix is elimination of the secured landfill as an ultimate disposal method (see Table 4). The objectives of the modified disposal approach is: 1) to decompose all hazardous organic spill residuals to innocuous end products and 2) to apply effective fixation processes to materials containing hazardous heavy metals to ensure permanent encapsulation of the metals under normal environmental conditions (e.g., burial in soil).

Biological and chemical treatment remains the first choice for reactive organics and this can be accomplished with conventional techniques. Unreactive and high hazard persistant organics show incineration as a first choice, but novel chemical and biochemical treatment methods will be available as options where a suitable incinerator is not available. The effectiveness of leaching techniques must be demonstrated in the case of mixtures with large quantitites of inert matter.

New technology cannot dispose of toxic inorganic materials; the toxic metals (ions) are elements and are not transmutable. Those materials that are toxic in all forms will remain a major disposal problem. Secured landfilling stands as the only option for these materials unless fixation processes are sufficiently effective to produce a nonharzardous residue that can go through normal disposal channels. In passing, one should recognize that in some cases toxicity resides in an element or its ions (Hg, As^{+3}, CO_4 $^{-2}$), in others the toxicity results from the structure of the chemical (PBC, HCN) where the elements can be rearranged into compounds that are generally not toxic (N_2, CO_2, NaCl). A few substances (phenyl mercuric acetate) have structural and elemental toxicity.

Based on the above considerations, future work must focus on three areas:

1) Economic alternatives to high temperature incineration;
2) Recovery or insolubilization techniques to remove the need for secure landfills; and
3) means of concentrating hazardous constituents from large volumes of inert substrates.

TABLE 4 AMENDED MATRIX FOR NOVEL DISPOSAL METHODS

Composition	Hazardous Organic Waste			Hazardous Inorganic Waste	
	Reactive	Unreactive	Highly Toxic/ Persistent+	Reactive	Highly Toxic/ Persistent+
Mixture with minor amounts of extraneous matter	B O	O S	O S	B	F-S**
Mixture with substantial amount of water	A-B A-O	A-O A-B	A-O A-B	B	A-F-S**
Mixtures with combustible solids	L*-B O	O L-B	O	B	F-F-S**
Mixtures with small non-combustible solids	L*-B L*-S	L-O L-B	L-O L-B	B	L-F-S**

+ = See Appendix A for listing
* = optional
**= not required if fixed product no longer meets hazardous waste criteria
B = Treatment (chemical or biochemical)
O = Incinerate
F = Fixation
A = Concentrate and remove from water
L = Leach
S = Secured landfill

SECTION 8

IMPACT OF REGULATIONS FROM RESOURCE CONSERVATION AND RECOVERY ACT

Many residual materials associated with the clean-up of hazardous material spills will by definition constitute hazardous wastes. While in the past this has suggested that certain legal constraints existed to prevent contamination of water and air through direct discharge, no regulations addressed these materials specifically, and little or no language addressed the use of land as a repository. Consequently, the bulk of these wastes (spill residuals included) were disposed of on the land--often indiscriminately. This option is no longer readily available. With passage of the Resource Conservation and Recovery Act (PL 94-580) and especially Title C of that Act, there is now a section of Federal law mandating the promulgation of rules, guidelines, and standards regulating the management of hazardous wastes. The implications of Title C are therefore of direct importance to spill residuals management and warrant a review.

Title C addresses hazardous waste management as one of the primary objectives of RCRA. It directs the EPA to identify which wastes are hazardous; the quantities, qualities, and concentrations of the wastes that are hazardous; and the forms of disposal that pose a threat to public health. Standards must also be issued for generators and transporters of hazardous wastes. These include record-keeping practices, labeling, selection of appropriate containers, use of a manifest system, and reporting of quantities and disposition. Coordination is required to ensure compatibility with transportation regulations (DOT, CFR Title 49).

Most importantly, persons owning or operating facilities for the treatment and storage of hazardous wastes are required to obtain permits within 90 days after identification and listing. Permit applications must indicate composition, quantities, the rate at which such wastes are to be disposed of, and the location of the disposal site. Permits can be revoked for noncompliance.

The Administrator must also publish guidelines to enable the states to develop approved hazardous waste programs. States with existing programs may receive interim (two-year) authorization to show that their programs are substantially equivalent to the Federal program. If non-conformities resurface, authorization can be withdrawn. To facilitate enforcement, the EPA and state officials are authorized to inspect facilities, copy records, and obtain samples as required.

While detailed guidelines and provisions have yet to be promulgated, proposed guidelines and regulations have been published in the Federal Register, Volume 43, No. 243, Monday, December 18, 1978. The impact of these regulations on spill residuals management must be considered. In the event of a spill and subsequent response activity, management of residuals will now require much greater attention to details. Only certified disposal contractors can be used. Residuals will have to be properly categorized and labeled. Manifest forms must be completed and submitted. In most cases, prior permission will also be required before residuals can be shipped to the disposal site. This will generally be the case, since as a "one-time" waste, the residuals will not have been listed in the permit application of the final permit granted to the site operator. In some of the states that have already initiated their own version of Title C (e.g., California, Minnesota) there are emergency variance provisions that can be invoked to bypass some of these time-consuming requirements and otherwise expedite movement of residuals to an acceptable site. It is entirely possible that, in a trade-off between immediate safety considerations and proper management, some residuals will still receive quick burial on-site; but these will be infrequent occurrences.

As noted, the specifics of requirments have not been finalized as this report is being prepared and may differ somewhat among states. Indeed, several states have proposed more restrictive definitions than those recommended by the EPA. It is therefore not possible to detail the required course of action for handling spill residuals from any given occurrences. Rather, response personnel must note that: 1) there will be regulatory requirements, both Federal and state, and 2) only certified or permitted contractors should be considered. Cognizance of these factors should stimulate proper inquiries at the time that disposal is contemplated. Since the Federal program is in the formation stages, no rosters are currently available to identify permitted disposal operators.

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APPENDIX A

SYMBOLS

Columns 1-3

X	Affirmative
(blank)	Negative
NR	No information available

Column 4

C	Potentially hazardous due to corrosivity
I	Potentially hazardous due to ignitability
R	Potentially hazardous due to reactivity
T	Potentially hazardous due to toxicity
X	Spill residues defined as hazardous in proposed RCRA regulations

C = pH ≤ 3 or ≥ 12.

I = Flash point < 60°C (140°F)
ASTM D-93-72 Pensy Martin closed cup.

R = Reactive, e.g., reacts with water and other common substances.

T = Toxic as As, Ba, etc.

APPENDIX A

LIST OF HAZARDOUS MATERIALS AND TREATMENT OPTIONS

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
ANTU	NR	NR	X		
Acetaldehyde	X	X	X		I
Acetic acid	X	X	X		C
Acetic anhydride	X	X	X		C
Acetone	X	X	X		I
Acetone cyanohydrin	X	X	X		X
Acetonitrile	X	X	X		I
Acetophenone	X	X	X		
Acetyl bromide	X	X	X		
Acetyl chloride	X	X	X		I
Acetylene	X		X		I
Acrolein	X	X	X		X
Acrylic acid	X	X	X		I
Acrylonitrile	X	X	X		X
Adiponitrile	X	X	X		
Alachlor	X	X	X		
Aldicarb	X	X	X		X
Aldrin			X	X	X
Allyl alcohol	X	X	X		I
Allyl chloride	X	X	X		I
Aluminum chloride		X			R
Aluminum fluoride		X			
Aluminum sulfate		X			
Aminoethanolamine	X	X	X		

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Ammonia	X	X	X		
Ammonium Compounds					
Ammonium acetate	X	X	X		
Ammonium benzoate	X	X	X		
Ammonium bicarbonate	X	X	X		
Ammonium bisulfite	X	X	X		
Ammonium bromide	X	X	X		
Ammonium carbamate	X	X	X		
Ammonium carbonate	X	X	X		
Ammonium chloride	X	X	X		
Ammonium citrate; dibasic	X	X	X		
Ammonium fluoborate	NR	NR			
Ammonium hydroxide	X	X			
Ammonium hypophosphite	X	X			
Ammonium iodide		X			
Ammonium nitrate	X	X			
Ammonium oxalate	X	X	X		
Ammonium pentaborate	X	X			
Ammonium perchlorate	X	X			
Ammonium persulfate	X	X			
Ammonium silicofluoride	NR	NR			
Ammonium sulfamate	X	X			
Ammonium sulfate	X				
Ammonium sulfide	X	X			
Ammonium sulfite	X	X			
Ammonium tartrate	X	X	X		
Ammonium thiocyanate	X	X			
Amyl acetate	X		X		I
Amyl alcohol	X		X		I
Aniline	X		X		X
Antimony Compounds					
Antimony pentachloride		X			R
Antimony pentafluoride		X			R
Antimony potassium tartrate		X			X
Antimony tribromide		X			R

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Antimony trichloride		X			R
Antimony trifluoride		X			R
Antimony trioxide		X			
Arsenic Compounds, Inorganic					
Arsenic acid		X		X	T
Arsenic disulfide		X		X	T
Arsenic pentaoxide		X		X	T
Arsenic trichloride		X		X	T
Arsenic trioxide		X		X	T
Arsenic trisulfide		X		X	T
Calcium arsenate		X		X	T
Potassium arsenate		X		X	T
Potassium arsenite		X		X	T
Sodium arsenate		X		X	T
Sodium arsenite		X		X	T
Asphalt blending stocks			X		
Roofers flux			X		
Asphalt			X		
Asphalt blending stocks			X		
Straight run residue			X		
Atrazine	NR	NR	X	NR	
Bacillus thuringus	X				X
Barium carbonate		X			T
Benzaldehyde	X		X		
Benzene	X		X		X
Benzoic acid	X	X	X		
Benzonitrile		X	X		
Benzoyl chloride	X	X	X		R
Benzyl chloride	X	X	X		R

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Beryllium Compounds					
Beryllium chloride		X			X
Beryllium fluoride		X			X
Beryllium nitrate		X			X
Bisphenol A	NR	NR	X		
Bromacil	NR	NR	X	NR	
Bromine		X			R
Butadiene, inhibited	NR		X		
Butane			X		I
1,4-Butanediol	NR		X		
1,4-Butendiol	NR		X		
Butyl acetate	X		X		I
n-Butyl acrylate	X		X		I
iso-Butyl acrylate	X		X		I
n-Butyl alcohol	X		X		I
sec-Butyl alcohol	X		X		I
tert-Butyl alcohol	X		X		I
Butylamine	X				I
Butylate	NR	NR		X	
Butylene			X		I
tert-Butyl hydroperoxide	NR	NR	X	X	I
1,4-Butynediol	NR	NR	X	X	
n-Butyraldehyde	X		X		I
iso-Butyraldehyde	X		X		I
Butyric acid	X		X		
Bux	NR	NR		NR	X
CDAA	NR	NR		NR	
Cacodylic acid	NR	NR		X	X

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Cadmium Compounds					T
Cadmium acetate		X		X	T
Cadmium bromide		X		X	T
Cadmium chloride		X		X	T
Calcium carbide		X			R
Calcium fluoride					
Calcium hydroxide		X			C
Calcium hypochlorite		X			
Calcium oxide		X			CR
Camphor oil	NR		X		
Captafol	NR	NR	X	NR	
Captan			X	NR	
Carbaryl	X	X	X	X	X
Carbofuran	NR	NR	X	NR	X
Carbon disulfide			X		
Carbon tetrachloride			X		X
Carbophenothion	NR	NR	X	NR	X
Chloramben	NR	NR	X	NR	
Chlordane			X	X	X
Chlorine		X		X	R
Chlorobenzene	X		X		X
Chlorobenzilate	NR	NR	X	NR	X
Chloroform	X		X		X
Chlorohydrins	NR	NR	X		
Chloropicrin	NR	NR	X		
Chloropropham (CIPC)	NR	NR	X	NR	
Chlorosulfonic acid		X			C

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Chromium Compounds					
Ammonium bichromate		X		X	T
Ammonium chromate		X		X	T
Calcium chromate		X		X	T
Chromic acetate		X		X	T
Chromic acid		X		X	T
Chromic sulfate		X		X	T
Chromous chloride		X		X	T
Chromyl chloride		X		X	T
Lithium bichromate		X		X	T
Lithium chromate		X		X	T
Potassium bichromate		X		X	T
Potassium chromate		X		X	T
Sodium bichromate		X		X	T
Sodium chromate		X		X	T
Strontium chromate		X		X	T
Zinc bichromate		X		X	T
Cobalt Compounds					
Cobaltous bromide		X			
Cobaltous fluoride		X			
Cobaltous formate		X			
Cobaltous sulfamate		X			
Copper Compounds					
Cupric acetate		X			
Cupric acetoaraonite		X			
Cupric chloride		X			
Cupric formate		X			
Cupric glycinate		X			
Cupric lactate		X			
Cu-naphthenates		X			
Cupric nitrate		X			R
Cupric oxalate		X			
Cupric subacetate		X			
Cupric sulfate		X			
Cupric sulfate, ammomated		X			
Cupric tartrate		X			
Cuprous bromide		X			

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Corn syrup	X	X	X		
Coumaphos	X	X	X		X
Cresol	X	X	X		
Creosote	NR	X	X		
Crotonaldehyde	NR	NR	X		I
Crufomate	NR	NR	X		X
Cumene	NR		X		I
Cyanide Compounds					
Barium cyanide	X	X		X	X
Calcium cyanide	X	X		X	X
Hydrogen cyanide	X	X	X	X	X
Potassium cyanide	X	X		X	X
Sodium cyanide	X	X		X	X
Zinc cyanide	X	X		X	X
Cyanogen bromide	X	X	X	X	X
Cyanogen chloride	X	X	X	X	X
Cyclohexane	X		X		I
Cyclohexanol	X		X		
Cyclohexanone	X		X		I
Cyclohexylamine	X		X		I
2,4-D (acid)	NR		X		X
2,4-D (esters)			X		X
DBCP	NR	NR	X	X	X
DCPA	NR	NR	X	NR	
DEET	NR	NR	X	NR	
DEF	NR	X	X	NR	
Dalapon	NR	NR	X	NR	
DDT			X	X	X
Decaldehyde	X		X		

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
1-decene	NR		X		
n-decyl alcohol	X		X		
Dextrose solution	X		X		
Diacetone alcohol	X		X	X	
Diazinon			X		X
Dibenzoyl peroxide	NR	NR	X		
Dibutylphthalate	X				
Dicamba	NR		X		
Dichlobenil	NR	NR	X		
Dichlone	NR	NR	X	NR	
Dichlorvos	NR	NR	X	NR	X
o-dichlorobenzene	X		X		X
p-dichlorobenzene	X		X		X
Dichlorodifluoromethane			X		X
Dichloromethane	X		X		
2,4-dichlorophenol			X		X
Dichloropropane	X		X		X
Dichloropropene	X		X		X
Dicofol	NR	NR	X	NR	X
Dicyclopentadiene	NR		X		I
Dieldrin			X	X	X
Diethanolamine	X		X		
Diethylamine	X		X		I
Diethylbenzene	X		X		I
Diethyl carbonate	X		X		I
Diethylene glycol	X		X		

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Diethylene glycol monoethylether	X		X		
Diethylene glycol monomethylether	X		X		
Diethylene glycol dimethylether	X		X		
Diethylenetriamine	X		X		
Diisobutylcarbinol	X		X		
Diisobutylene	NR		X		
Diisopropanolamine	X		X		
Dimethoate	NR	NR	X	NR	X
Dimethylamine	X		X		I
Dimethylformamide	X		X		
1,1-dimethylhydrazine	X		X		I
Dimethylsulfate	NR	NR	X		
Dimethylsulfoxide	NR	NR	X		
Dinoseb	X	NR	X	X	X
2,4-dinitroaniline			X		X
Dinitrobenzene			X		X
Dinitrophenol			X		
Dioctyladipate	NR	NR	X		X
Dioctylphthalate	NR	NR	X		I
1,4-dioxane	NR	NR	X		
Diphenamid	NR	NR	X		
Diphenylmethane	NR	NR	X		
Diisocyanate	NR	NR	X	X	
Dipropylene glycol	X		X		
Diquat	NR		X		

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Distillates: flashed feed stocks	X		X		I
Distillates: straight run	X		X		I
Disulfoton	NR	NR	X	X	X
Dithiocarbamates	NR	NR	X	X	
Diuron	NR	NR	X		
Dodecene	X		X		
1-dodecene	X		X		
Dodecanol	X		X		
Dodecylbenzenesulfonic acid	X		X		
Dodecylbenzenesulfonic acid, calcium salt	X		X		
Dodecylbenzenesulfonic acid, taopropanolamine salt	X		X		
Dodecylbenzenesulfonic acid, sodium salt	X		X		
Dodecylbenzenesulfonic acid, triethanotamine salt	X		X		
Dodine	NR	NR	X	NR	
Dowtherm	NR	NR	X		
Dursban			X	NR	X
Dyfonate	NR	NR	X	NR	X
EPTC	NR	NR	X		
Endosulfan			X	NR	X
Endothall	NR	NR	X	NR	
Endrin			X	X	X
Epichlorohydrin	NR	NR	X		I
Epoxidized vegetable oils	NR	NR	X		

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Ethane			X	I	
Ethion	NR		X	NR	X
Ethoxylated dodecanol	X		X		
Ethoxylated pentadecanol	X		X		
Ethoxylated tetradecanol	X		X		
Ethoxylated tridecanol	X		X		
Ethoxy triglycol	X		X		
Ethyl acetate	X		X		I
Ethyl acrylate	X		X		I
Ethyl alcohol	X		X		I
Ethylbenzene	X		X		I
Ethyl butanol	X		X		I
Ethyl chloride	X		X		I
Ethylene					I
Ethylene cyanohydrin	NR	NR	X		R
Ethylenediamine	X	X	X		I
Ethylenediamine, tetraacetic acid	X	X	X		
Ethylene dibromide	NR		X		X
Ethylene dichloride	NR		X		I
Ethylene glycol monoethylether acetate	X		X		
Ethylene glycol dimethylether	X		X		
Ethylene glycol monoethylether	X		X		
Ethylene glycol	X		X		
Ethylene glycol monobutyl ether	X		X		I
Ethylene glycol monomethylether	X		X		I
Ethyleneimine	X		X		

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Ethylene oxide					I
Ethylether	X		X		I
Ethyl hexandiol	NR	NR	X	X	
2-ethyl hexanol	X		X		
Ethyl hexyl tallate	X		X		
2-ethyl-3-propylacrolein	X		X		
Fenitrothion	NR	NR	X		X
Fensulfothion	NR	NR	X		X
Ferrous sulfate		X			
Fluometuron	NR	NR	X		
Fluorine		X		X	X
Fluorine Compounds					
Aluminum fluoride		X			
Ammonium bifluoride	X	X			
Ammonium fluoride	X	X			
Hydrofluoric acid		X			
Sodium bifluoride		X			
Sodium fluoride		X			
Stannous fluoride		X			
Folex	NR	NR	X	NR	
Folpet	NR	NR	X	NR	
Formaldehyde	X		X		X
Formic acid	X	X	X		
Fumaric acid	X		X		
Furfural	X		X		
Gas oil: cracked	X		X		I
Gasoline blending stocks: alkylates	X		X		I

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Gasolines: automative (<4.23 g lead/gal)	X		X		I
Gasolines: aviation (<4.86 g lead/gal)	X		X		I
Gasolines: casinghead	X		X		I
Gasolines: polymer	X		X		I
Gasoline blending	X		X		I
Stocks: reformates					I
Gasolines: straight run	X		X		I
Glycerine	X		X		
Glycidylmethacrylate	X		X		
Guthion	X	X	X	X	X
Heliotropin acetal	NR	NR	X	NR	
Heptachlor			X	X	X
Heptane	X				I
Heptanol	X		X		I
1-heptene			X		
Hexamethylenediamine	X		X		
Hexamethylenetetramine	X		X		
Hexane	X		X		I
Hexanol	X		X		
1-hexene	X		X		I
Hexylene glycol	X		X		
Hydrazine	X		X		I
Hydrochloric acid		X			C
Hydrogen peroxide		X			R
Hydrogen sulfide		X			I
Hydroxylamine	X	X	X		I

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Iron Compounds					
Ferric ammonium citrate	X	X	X		
Ferric ammonium oxalate	X	X	X		
Ferric chloride		X			C
Ferric fluoride		X			
Ferric nitrate		X			C
Ferric sulfate		X			C
Ferrous ammonium sulfate		X			
Ferrous chloride		X			
Ferrous sulfate		X			
Isoamylalcohol	X		X		I
Isobutane					I
Isobutylalcohol	X		X		I
Isobutylene					I
Isodecaldehyde	X		X		
Isodecylalcohol	X		X		
Isohexane	X		X		I
Isooctaldehyde	X		X		
Isooctylalcohol	X		X		
Isopentane	X		X		I
Isoprene	X		X		I
Isopropylacetate	X		X		I
Jet fuels: JP-4	X		X		I
Jet fuels: JP-1 (kerosene)	X		X		I
Jet fuels: JP-3	X		X		I
Jet fuels: JP-5 (kerosene, heavy)	X		X		I
Kerosene	X		X		I
Kerthane	X		X		
Latex, liquid synthetic	X		X		

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Lauryl mercaptan	X		X		
Lead Compounds					T
Lead acetate		X		X	T
Lead arsenate		X		X	X
Lead chloride		X		X	T
Lead fluoborate		X		X	T
Lead fluoride		X		X	T
Lead iodide		X		X	T
Lead nitrate		X		X	T
Lead stearate		X		X	T
Lead sulfate		X		X	T
Lead sulfide		X		X	T
Lead tetraacetate		X		X	T
Lead thiocyanate		X		X	T
Lead thiosulfate		X		X	T
Lead tungstate		X		X	T
Lindane			X	X	X
Linear alochols (12-15 carbons)	X		X		I
Linuron	NR	NR	X	X	
Liquefied natural gas					I
Liquefied petroleum gas					I
Lithium aluminum hydride		X			R
MGK-264	NR	NR	NR	X	X
MGK-326	NR	NR	NR	X	
MSMA	NR	NR	NR	X	
Maleic hydrazide	NR	NR	X		
Malathion		X	X	X	X
Maleic acid	X	X	X		
Maleic anhydride	X	X	X		
Mercury		NR		X	T

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Mercury Compounds					T
Mercuric acetate		X		X	T
Mercuric cyanide		X		X	T
Mercuric nitrate		X		X	T
Mercuric sulfate		X		X	T
Mercuric thiocyanate		X		X	T
Mercurous nitrate		X		X	T
Metaldehyde	NR	NR	X	NR	I
Methane					I
Methanearsonic acid	NR	NR		X	T
Sodium Salts	NR	NR	X		T
Methomyl	NR	NR	X	NR	X
Methoxychlor			X		X
Methyl acrylate	X		X		I
Methyl alcohol	X		X		I
Methyl amyl acetate	X		X		I
Methyl amyl alcohol	X		X		I
Methyl bromide					X
Methyl chloride					I
Methylethylketone	X		X		I
Methylethylpyridine	X		X		
Methylisobutylcarbinol	X		X		I
Methylisobutylketone	X		X		I
Methyl mercaptan	X		X		I
Methyl methacrylate	X		X		I
Methyl parathion	X		X		X
Mevinphos			X		X
Mineral spirits	X		X		I

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Monochlorodifluoromethane					
Monocrotophos	NR	NR	X	X NR	X
Monoethanolamine	X	X	X		
Monoethylamine	X	X	X		
Monoisopropanolamine	X	X	X		
Monomethylamine	X	X	X		
Morpholine	X		X		I
Naptalam	NR	NR	X	X NR	
Naphtha: coal tar	X		X		I
Naphthalene	X		X		X
Naphtha: solvent	X		X		I
Naphtha: stoddard solvent	X		X		I
Naphtha: VM & P (75% naphtha)	X		X		I
Naphthenic acid	X	X	X		
Nickel Compounds					
Nickel ammonium sulfate		X			
Nickel chloride		X			
Nickel formate		X			
Nickel hydroxide		X			
Nickel nitrate		X			
Nickel sulfate		X			
Nicotine	NR	NR	X		X
Nitralin	NR	NR	X	X NR	
Nitric acid	X	X	X		R
Nitrobenzene	X		X		
Nitrogen dioxide					X
Nitromethane			X		I
Nitrophenol			X		X

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Nitrosylchloride	NR	NR	NR		
Nonanol	X		X		
Nonene	X		X		
1-nonene	X		X		
Nonylphenol	X		X		
Norbormide	NR	NR	X	NR	
Norea	NR	NR	X	X	
Octanol	X		X		
1-octene	X		X		
Oils: clarified	X		X		I
Oils: crude	X		X		
Oils: diesel	X		X		I
Oils, edible: castor	X		X		I
Oils, edible: cottonseed	X		X		
Oils, edible: fish	X		X		
Oils, edible: olive	X		X		
Oils, edible: peanut	X		X		
Oils, edible: soyabean	X		X		
Oils, edible: vegetable	X		X		
Oils, fuel: no. 1 (kerosene)	X		X		I
Oils, fuel: no. 1-D	X		X		I
Oils, fuel: no. 2	X		X		I
Oils, fuel: no. 2-D	X		X		I
Oils, fuel: no. 4	X		X		I
Oils, fuel: no. 5	X		X		I
Oils, Fuel: no. 6	X		X		
Oils, Miscellaneous: absorption	X		X		

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Oils, miscellaneous: coal tar	X		X		I
Oils, miscellaneous: lubricating	X		X		
Oils, miscellaneous: mineral	X		X		
Oils, miscellaneous: mineral seal	X		X		
Oils, miscellaneous, motor	X		X		
Oils, miscellaneous: neatsfoot	X		X		
Oils, miscellaneous, penetrating	X		X		
Oils, miscellaneous: range	X		X		
Oils, miscellaneous: resin	X		X		
Oils, miscellaneous: road	X		X		
Oils, miscellaneous: rosin	X		X		
Oils, miscellaneous: sperm	X		X		
Oils, miscellaneous: spindle	X		X		
Oils, miscellaneous: spray	X		X		
Oils, miscellaneous: tall	X		X		
Oils, miscellaneous: tanner's	X		X		
Oils, miscellaneous: transformer			X	X	X
Oxalic acid	X	X	X		
PCNB	NR	NR	NR	NR	X
Paraformaldehyde	X		X		
Paraquat	NR	NR	X	NR	
Parathion	X		X	X	X
Pentachlorophenol			X		X

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Pentadecanol	X		X		
Pentane			X		I
1-pentene			X		I
Petrolatum	X		X		
Petroleum naphtha			X		I
Phenol	X		X		
Phorate	NR	NR	X	NR	X
Phosgene					X
Phosphoric acid		X			C
Phosphorus	NR	NR			R
Phosphorus oxychloride	NR	NR			R
Phosphorus pentasulfide	NR	NR			R
Phosphorus trichloride	NR	NR			R
Phthalic anhydride	X		X		
Picloram	NR		X	NR	
Pindone	NR	NR	X	X	X
Piperonyl butoxide	NR	NR	X		
Polyacrylonitrile				X	
Polychlorinated biphenyls.			X	X	X
Polyhedrivirus	NR	NR	X		
Polyphosphoric acid		X			
Polypropylene glycol	X		X		
Methylether			X		
Potassium hydroxide		X			C
Potassium iodide		X			
Potassium permanganate		X			R
Propachlor	NR	NR	X	NR	

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Propane					I
Propanil	NR	NR	X	NR	
Propazine	NR	NR	X	NR	
Propionaldehyde	X		X		I
Propionic acid	X	X	X		I
Propionic anhydride	X	X	X		
Propyl alcohol	X		X		I
Propylene					I
Propylene butylene polymer			X		
Propylene glycol	X		X		
Propylene glycol methylether	X		X		I
Propylene oxide					I
Propylenetetramer	X		X		
Pyrethrine			X		X
Pyridine	X		X		I
Quinotine			X		
Resorcinol			X		
Ronnel	NR	NR	NR	X	X
Rotenone	NR	NR	X	X	X
Selenium oxide		X			T
Silver nitrate		X			T
Silvex	NR	NR	X		
Simazine	NR	NR	X		
Sodium		X		R	R
Sodium alkyl benzenesulfonates	X		X	R	
Benzenesulfonates					
Sodium alkylsulfates	NR	NR	X		

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Sodium amide	NR	NR	NR		R
Sodium bisulfite		X			
Sodium borohydride		NR			
Sodium chlorate		X			R
Sodium ferrocyanide		X			
Sodium fluoracetate	NR	NR			
Sodium hydride		X			R
Sodium hydrosulfide		X			
Sodium hydroxide		X			C
Sodium hypochlorite		X			
Sodium methylate	X	X	X		
Sodium nitrite		X			
Sodium phosphate, dibasic		X			
Sodium phosphate, monobasic		X			
Sodium phosphate, tribasic		X			
Sodium selenite		X			
Sodium silicate		X			
Sodium sulfide		X			
Sodium sulfite		X			
Sorbitol	X		X		
Strychnine	NR	NR	X		X
Styrene	X		X		I
Sulfolane	NR				
Sulfur (liquid)					R
Sulfur dioxide		X			T
Sulfuric acid		X			O
Sulfur monochloride		X			R

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Sulfurylchloride		X			R
2,4,5-T (acid)			X		T
2,4,5-T (esters)			X	X	T
TBA	NR	NR	X	X	
TCP and salts	NR	NR	X	X	
TDE			X	X	X
Tallow	X		X		
Tetrachloroethylene			X		X
Tetradecanol	X		X		
1-tetradecene	X		X		
Tetraethyl lead			X	X	X
Tetraethyl pyrophosphate		X	X		X
Tetrahydrofuran			X		I
Tetrahydronaphthalene			X		
Tetramethyl lead		X	X	X	I
Titanium tetrachloride		X			R
Toluene	X		X		I
Toluene 2,4-dissocyanate	NR	NR	X		T
Toxaphene			X	X	X
Trichlorfon			X		X
Trichloroethane	NR	NR	X		X
Trichloroethylene	NR	NR	X		X
Trichlorofluoromethane	NR	NR	X		X
Trichlorophenol			X	X	X
Tricresyl phosphate	NR	NR	X		
Tridecanol	X		X		

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
1-tridecene	X		X		
Triethanolamine	X		X		
Triethylamine	X	X	X		I
Triethylbenzene	X		X		
Triethylene glycol	X		X		
Triethylenetetramine	X		X		
Trifluralin	NR	NR	X	NR	
Trimedlure	NR	NR	X	X	
Trimethylamine	X		X		
Turpentine	X		X		I
Undecanol	X		X		
1-undecene	X		X		
Uranium Compounds					
Uranium peroxide		X			
Uranyl acetate		X			
Uranyl nitrate		X			
Uranyl sulfate		X			
Urea	X	X	X		
Valeraldehyde	X		X		I
Vanadium Compounds					
Vanadium pentoxide		X			
Vanadyl sulfate		X			
Vernolate	NR	X	X	X	
Vinyl acetate	X		X		I
Vinyl chloride	NR	NR	X		X
Vinylidenechloride inhibited	NR	NR	X		I
Vinyltoluene	NR	NR	X		I
Warfarin	NR	NR	X		

Common Name	Amenable to Conventional Biological Treatment	Amenable to Aqueous Chemical Treatment	Amenable to Incineration	Highly Toxic and Persistent	RCRA Defined Hazardous
Waxes: carnauba	X		X		
Waxes: paraffin			X		
Xylene	X		X		I
Xylenol	X		X		
Zectran			X		X
Zinc Compounds					
Zinc acetate		X			
Zinc ammonium chloride		X			
Zinc borate		X			
Zinc bromide		X			
Zinc carbonate		X			
Zinc chloride		X			
Zinc fluoride		X			
Zinc formate		X			
Zinc hydrosulfite		X			
Zinc nitrate		X			
Zinc phenolsulfonate		X			
Zinc phosphide		X			
Zinc potassium chromate		X			R
Zinc silicofluoride		X		X	X
Zinc sulfate		X			
Zinc sulfate, monohydrate		X			
Zirconium Compounds					
Zirconium acetate		X			
Zirconium potassium fluoride		X			
Zirconium nitrate		X			
Zirconium oxychloride		X			
Zirconium sulfate		X			R
Zirconium tetrachloride		X			R

APPENDIX B

DESCRIPTION AND OPERATION OF INCINERATORS

LIQUID INCINERATORS

Horizontally Fired

Monsanto operates a liquid injection incinerator to dispose of inhouse liquid wastes and contaminated PCB's from customers. It is located at Monsanto's Krummrich Plant at East St. Louis, Illinois.

The incinerator is a liquid injection type housed in a horizontal cylinder 20 ft long and 9.5 ft in diameter. High pressure steam is used to atomize the waste liquid and inject it into the liquid combustor. The typical feed rate is 2 gal/min. An additional burner uses natural gas as an auxiliary fuel. The operating temperatures vary from 2000 to 2200°F. The outer cylindrical shell is protected from the heat by a lining of refractory brick. A blower supplies 25% excess air forcing the fumes from the plenum and through an oxidizer. The residence time in the oxidizer is 2 to 3 sec.(1)* The fumes leave the oxidizer and enter a water quench column that reduces the temperature of the hot fumes. Particulates are removed in a high energy venturi scrubber. Finally, acidic emissions are removed in a packed-bed scrubber at the base of the stack. The stack is 40 ft high and equipped with a demister.

A large majority of the wastes burned in the Monsanto incinerator are PCB derivatives from process still bottoms and contaminated transformer oils. The heating value of the waste is about 9000 Btu/lb. Phosphorus compounds can not be burned because of the formation of particulates (P^2O_5) that are not efficiently collected by the system. The incinerator is not equipped to handle suspended solids.

A typical liquid incineration system is shown in Figure B-1. This unit is operated by Dow Chemical Company at their Midland, Michigan plant. It is similar to the Monsanto incinerator described previously. The unit has a combustion chamber 35 ft long and 10 ft square in cross section.

Liquid wastes are fed through a combination of four dual-fired nozzles. The exhaust gases are quenched in a spray chamber and scrubbed in a high energy venturi scrubber and a packed-bed scrubber equipped with

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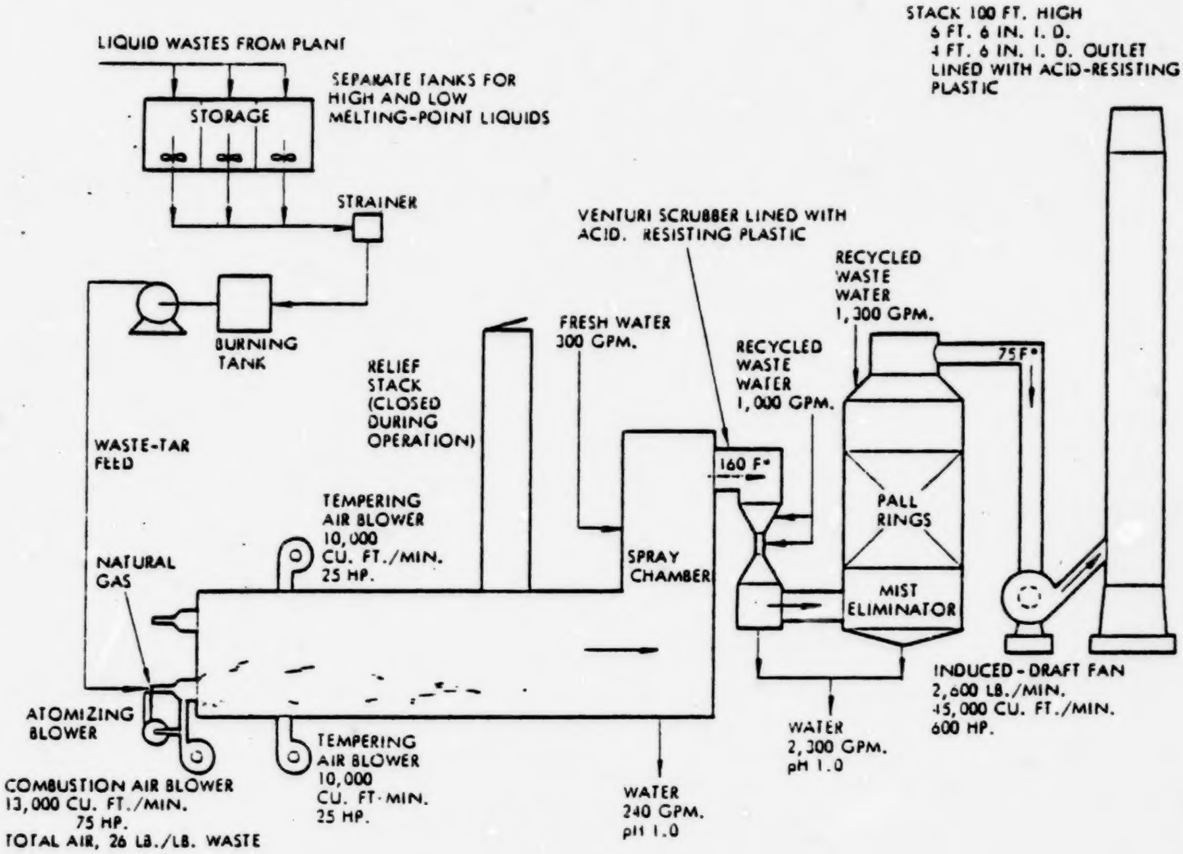
*Cited references are listed at the end of this appendix ("B").


LIQUID WASTES FROM PLANT
STORAGE
SEPARATE TANKS FOR HIGH AND LOW MELTING-POINT LIQUIDS
STRAINER
BURNING TANK
WASTE-TAR FEED
NATURAL GAS
ATOMIZING BLOWER
COMBUSTION AIR BLOWER
13,000 CU. FT./MIN.
75 HP.
TOTAL AIR, 26 LB./LB. WASTE
TEMPERING AIR BLOWER
10,000 CU. FT./MIN.
25 HP.
TEMPERING AIR BLOWER
10,000 CU. FT-MIN.
25 HP.
RELIEF STACK (CLOSED DURING OPERATION)
FRESH WATER 300 GPM.
SPRAY CHAMBER
WATER 240 GPM. pH 1.0
VENTURI SCRUBBER LINED WITH ACID. RESISTING PLASTIC
160 F°
RECYCLED WASTE WATER 1,000 GPM.
RECYCLED WASTE WATER 1,300 GPM.
PALL RINGS
MIST ELIMINATOR
WATER 2,300 GPM. pH 1.0
75F°
STACK 100 FT. HIGH
6 FT. 6 IN. I. D.
4 FT. 6 IN. I. D. OUTLET
LINED WITH ACID-RESISTING PLASTIC
INDUCED - DRAFT FAN
2,600 LB./MIN.
45,000 CU. FT./MIN.
600 HP.

WASTE TAR FEED: AVG. 10 GPM.
13,00 BTU.. LB.
TEMPERATURE 80-1000C.
VISCOSITY 150 SSU.

5 PSI FEED
4 BURNERS, COMBUSTION
GAS AND TAR NOZZLES
5/16 - IN.ORIFICE

Figure B-1. Diagram of horizontal liquid waste incinerator.

a mist eliminator. An induced draft fan draws the gases and vapors through the system and forces the clean gas out from the 100 ft stack.(2,3)

Many of the liquid wastes treated in the Dow facility are solids at room temperature and must be kept hot in order to remain liquid. Most of the wastes are chlorinated hydrocarbons and can contain as much as 50 wt% chlorine.(2,3)

Vertically Fired

Figure B-2 shows a vertically fired liquid waste incinerator. This unit is designed and sold by Prenco Division of Picklands Mather and Company.(4) After the retort is brought to operating temperature (1600 to 3000°F) by burning natural gas, liquid waste is admitted to the air-waste entrainment compartment. The aerated waste moves to the turbulence compartment where it is mixed with more air and injected into the high-temperature retort. The exhaust gases and any inert particles produced flow vertically through the air cone and out the top of the retort. To handle hazardous wastes, secondary treatment equipment would be required just as with the horizontal liquid combustors.

SOLID INCINERATORS

Fluidized Bed Incinerators(5,6,7, 8,)

Fluidized bed technology from the petroleum and chemical processing industries has been adapted to the incineration of wasters. The most common application involves the disposal of sludges or slurried wastes. A flow diagram for a typical solids disposal system utilizing fluid bed incineration is shown in Figure B-3. The major processing steps are listed below:

1. Grit removal to protect unit from abrasion
2. Sludge thickening
3. Solids size reduction
4. Dewatering
5. Incineration
6. Exhaust gas treatment and ash disposal.

A typical fluidized bed incinerator is shown in Figure B-4. The reactor operates at a pressure of about 2 psig and a temperature of 1400 to 1500°F. When sand is used as the bed material the maximum temperature is limited to 2000°F.(9) Lower temperature operation is avoided to ensure odor control. The sludge is fed at the bottom of the reactor just above the distributor plate. Fluidizing air enters below the distributor plate. The sludge is dried and oxidized. Much of the heat of combustion is transferred to the sand bed. The combustion gases and the ash leave at the top of the reactor. An auxiliary burner is used to heat the bed to temperature prior to feeding sludge. Once the unit has reached the proper operating tempeature this auxiliary burner may be operated at partial fire to incinerate low heat-of-combustion liquid or gaseous wastes.

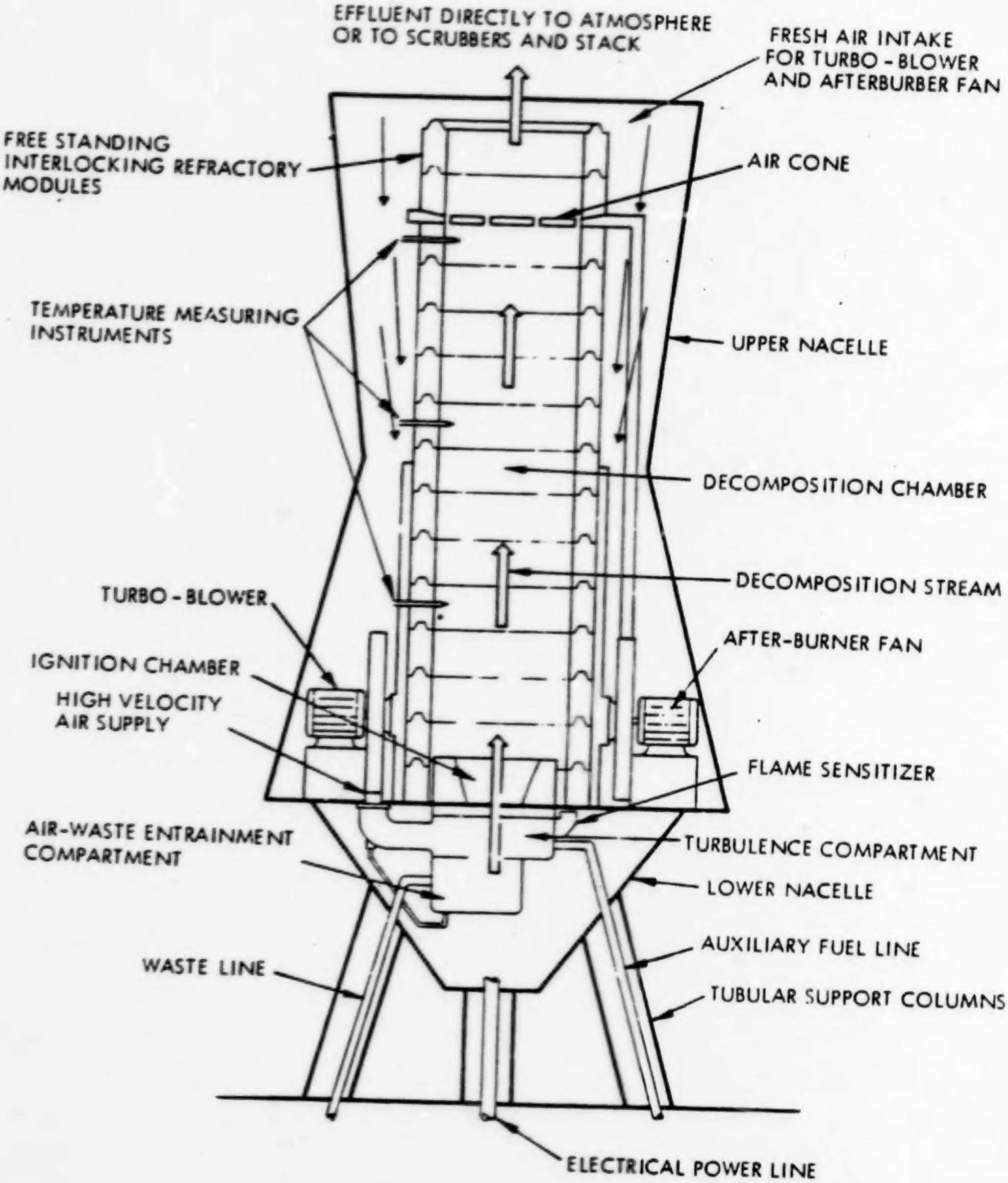

EFFLUENT DIRECTLY TO ATMOSPHERE OR TO SCRUBBERS AND STACK
FRESH AIR INTAKE FOR TURBO - BLOWER AND AFTERBURBER FAN
FREE STANDING INTERLOCKING REFRACTORY MODULES
AIR CONE
TEMPERATURE MEASURING INSTRUMENTS
UPPER NACELLE
DECOMPOSITION CHAMBER
DECOMPOSITION STREAM
TURBO - BLOWER
AFTER-BURNER FAN
IGNITION CHAMBER
HIGH VELOCITY AIR SUPPLY
FLAME SENSITIZER
AIR-WASTE ENTRAINMENT COMPARTMENT
TURBULENCE COMPARTMENT
LOWER NACELLE
AUXILIARY FUEL LINE
WASTE LINE
TUBULAR SUPPORT COLUMNS
ELECTRICAL POWER LINE

Figure B-2. Typical vertically fired liquid waste incinerator.

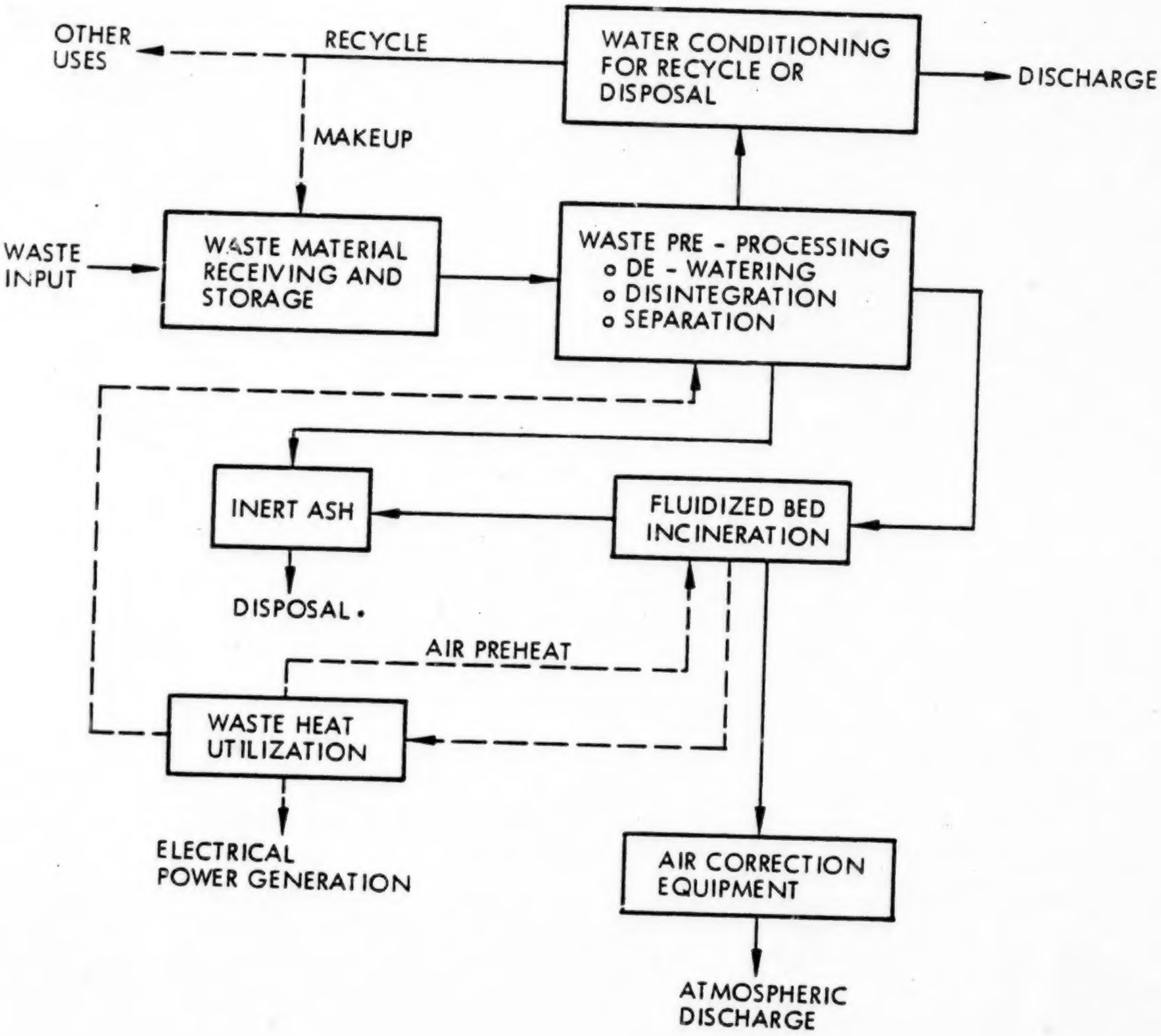

OTHER USES
RECYCLE
WATER CONDITIONING FOR RECYCLE OR DISPOSAL
DISCHARGE
MAKEUP
WASTE INPUT
WASTE MATERIAL RECEIVING AND STORAGE
WASTE PRE - PROCESSING
o DE - WATERING
o DISINTEGRATION
o SEPARATION
INERT ASH
FLUIDIZED BED INCINERATION
DISPOSAL.
AIR PREHEAT
WASTE HEAT UTILIZATION
ELECTRICAL POWER GENERATION
AIR CORRECTION EQUIPMENT
ATMOSPHERIC DISCHARGE

Figure B-3. Flow diagram for sludge disposal by fluidized bed incineration.

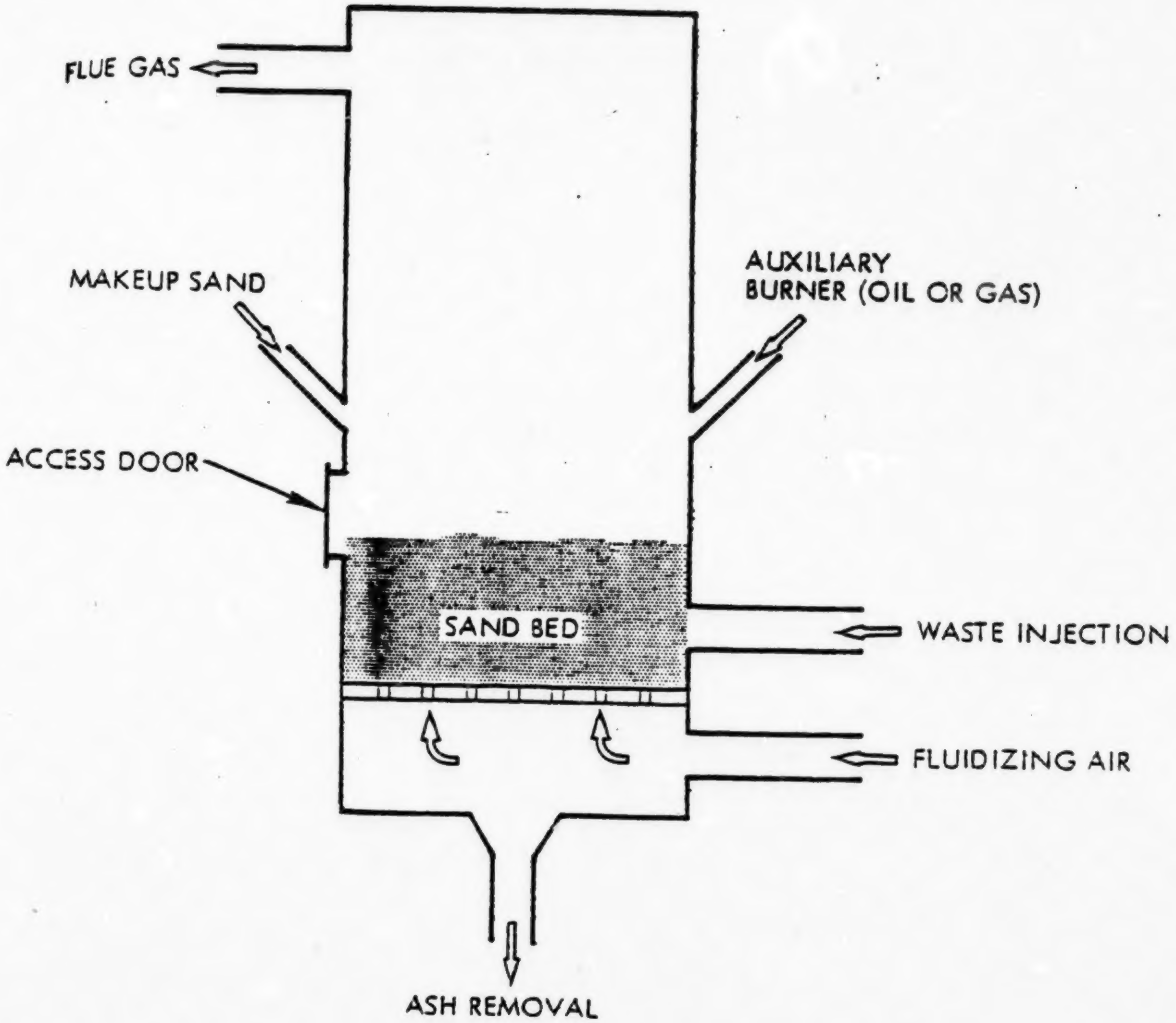

FLUE GAS
MAKEUP SAND
AUXILIARY BURNER (OIL OR GAS)
ACCESS DOOR
SAND BED
WASTE INJECTION
FLUIDIZING AIR
ASH REMOVAL

Figure B-4. Fluidized Bed Incinerator.

Fluidized bed incinerators are relatively new and are becoming increasingly popular for sludge incineration. Some of the advantages of these units are: 1) good mixing of sludge and air, 2) no moving parts (requires less maintenance), 3) heat exchange within the sand bed (requires fewer heat exchanges for efficient operation), and 4) sand bed service as a heat reservoir (permitting intermittent operation without excessive heatup).(5)

Multiple Hearth Incinerators(5,6,7,8)

The multiple hearth incinerator is widely used as an incineration system because of its simplicity, durability, and flexibility. This type of unit was initially designed to incinerate sewage plant sludges in 1934 and has been used quite successfully in this application.(2)

A flow sheet for a typical waste disposal plant with a multiple hearth incinerator is shown in Figure 3 (Refer to main text, Chapter 5). The solid waste is degritted and dewatered before it is fed to the incinerator. The exhaust gases are scrubbed prior to release to the atmosphere. Ash is removed to a landfill.

The incinerator consists of a refractory-lined circular steel shell with refractory hearths located one above the other. Solid waste or partially dewatered sludge is fed to the top of the unit, where a rotating central shaft plows it across the hearth to drop holes. The uncombusted material falls to the next hearth and the process is repeated until, eventually, ash is discharged at the bottom. Combustion air flows countercurrent to the sludge; the exhaust gases exit at the top of the incinerator. In the upper zone of the incinerator the incoming solid waste or sludge is heated by the hot exhaust gases. Temperatures of approx. 1000°F are typical in this zone. In the middle zone volatile gases and solids are burned at temperatures of 1600 to 1800°F. In the lower zone, fixed carbon burns at temperatures around 600°F.(8)

An auxiliary burner is usually available for oxidizing low energy, alternative wastes including liquids and solids.

Rotary Kiln Incinerators(6,8)

Rotary kilns are versatile units that have been used to dispose of various solid and liquid wastes including chemical refuse, paper, wood, obsolete chemical warfare agents, munitions, and chlorinated hydrocarbons.(2,4,6) Kilns have been utilized in both industrial and municipal installations and are not typically used as sewage sludge incineration units.

Figure B-6 shows a rotary kiln incineration facility that is operated by Dow Chemical Company at Midland, Michigan. Solid waste is dumped into the refuse pit where an overhead crane mixes it and raises it to the charging hopper. While the solid waste is being fed, liquid wastes are atomized with air and steam and are fired horizontally into the kiln. As the refuse moves down the kiln the organic matter is destroyed and only

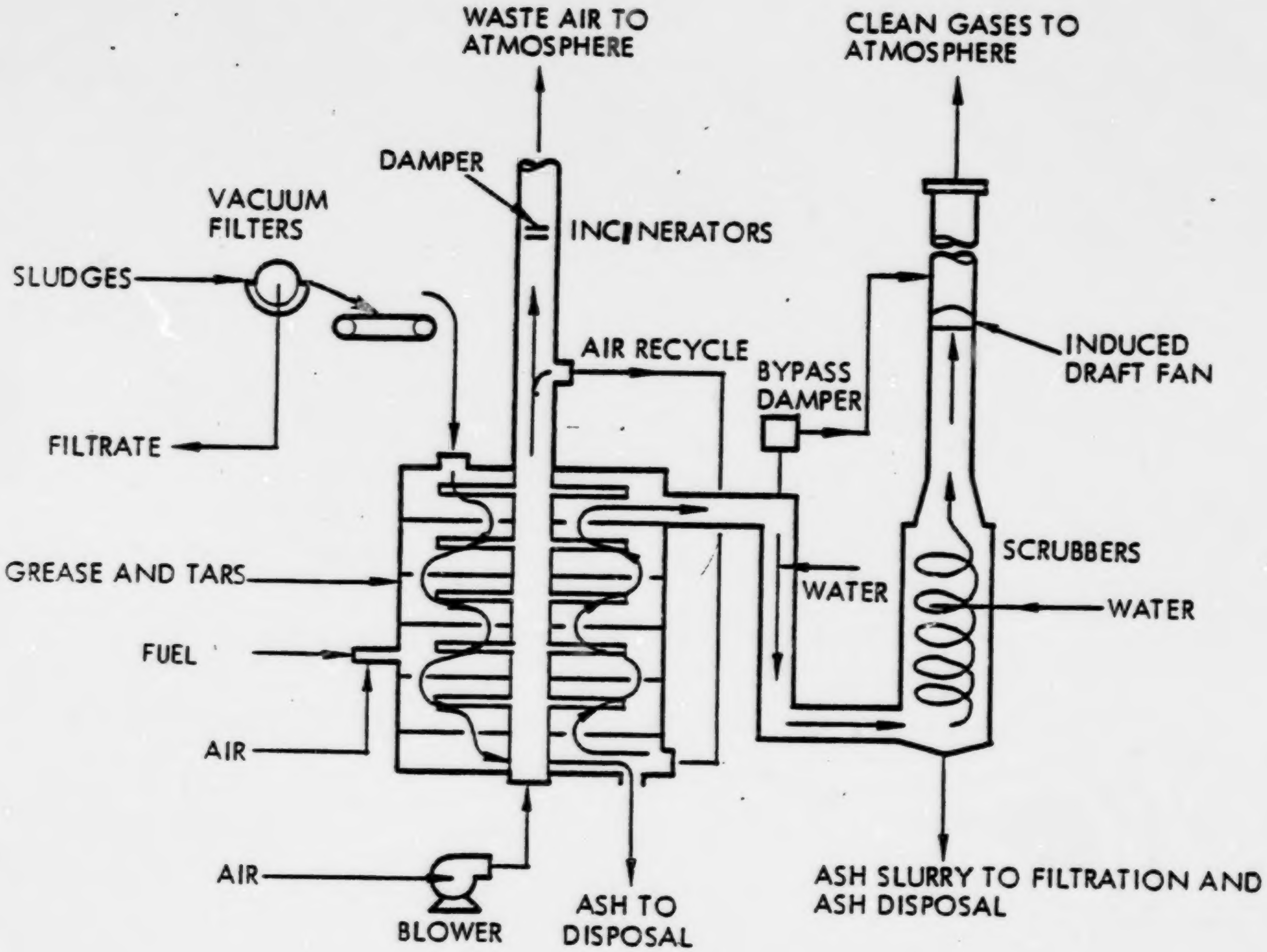

WASTE AIR TO ATMOSPHERE
CLEAN GASES TO ATMOSPHERE
DAMPER
VACUUM FILTERS
INCINERATORS
SLUDGES
AIR RECYCLE
BYPASS DAMPER
INDUCED DRAFT FAN
FILTRATE
GREASE AND TARS
SCRUBBERS
WATER
WATER
FUEL
AIR
AIR
BLOWER
ASH TO DISPOSAL
ASH SLURRY TO FILTRATION AND ASH DISPOSAL

Figure B-5. Multiple hearth incinerator.

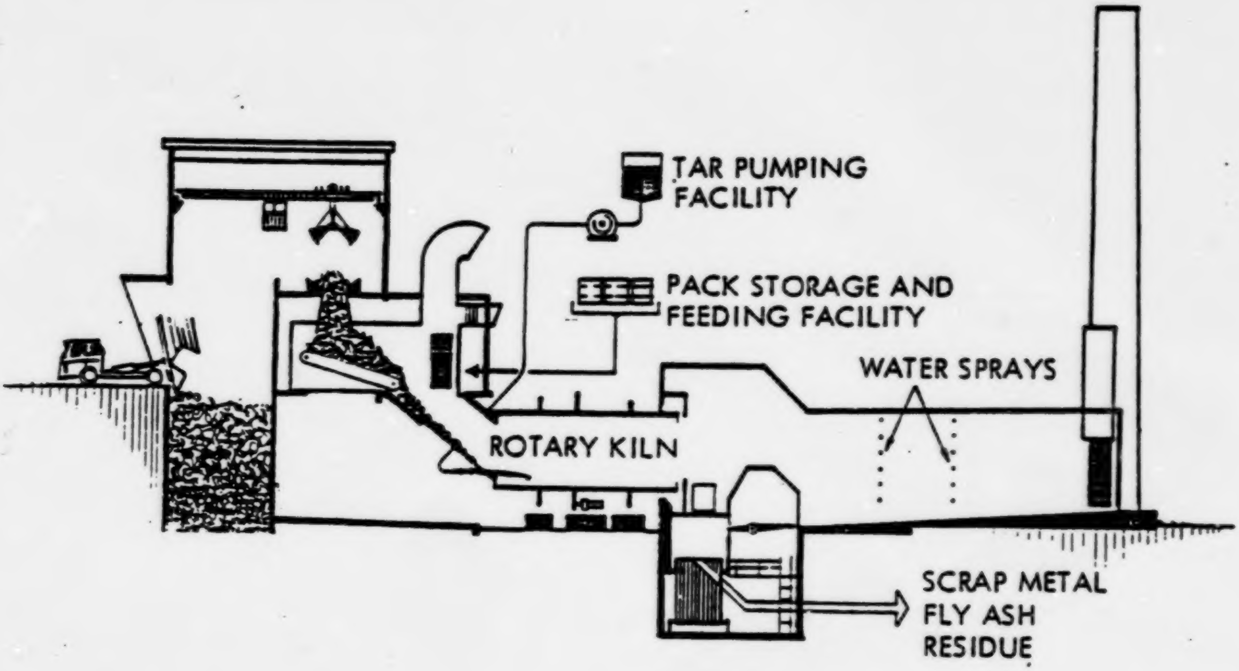

TAR PUMPING FACILITY
PACK STORAGE AND FEEDING FACILITY
WATER SPRAYS
ROTARY KILN
SCRAP METAL
FLY ASH
RESIDUE

Figure B-6. Rotary kiln incinerator

an inorganic ash remains. The ash is discharged from the end of the kiln into a conveyor trough that contains 3 ft of water. After quenching, the ash is conveyed to a dumping trailer and hauled to a landfill.

After leaving the kiln, the gaseous and vapor products of combustion enter the secondary combustion chamber and impinge on refractory surfaces. No secondary fuel or afterburners are used. Combustion gases are scrubbed in a spray tower and then exhausted to the atmosphere through a stack.(2)

The kiln itself is a cylindrical shell lined with refractory and mounted with its axis at a slight angle to the horizontal. Rotary kilns are highly efficient when applied to solids, liquids, sludges, and tars as it attains excellent mixing of unburned waste and oxygen as it revolves. Temperatures in the kiln range from 1600 to 3000°F and residence times from seconds (gases) to hours (solids) depending on the feed material.

GAS INCINERATORS

Direct Flame Incineration

Direct flame incineration is normally used with materials that are at or near their lower limit of combustion. In a well-designed combustor or burner, gases having a heating value as low as 100 BTU/ft^3 can be burned without auxiliary fuel.

Less combustible mixtures of organic material and air (heating values of the order of 1-20 BTU/ft^3) can be injected along with an auxiliary fuel directly through a burner. However, most conventional industrial burners require temperatures of 2200°F or greater to sustain combustion and the amount of natural gas required is quite high. Since temperatures of only 1000 to 1500°F are needed for thermal incineration, it is often more economical to heat a combustion chamber using a conventional fuel in an industrial burner and then to inject the dilute gas into the chamber just downstream of the flame.

Most waste gas incineration problems involve mixtures of organic material and air in which the organic material loading is very small. Related to hazardous waste spills it may sometimes be desirable to separate the waste from the spill substrate by drying (vaporization). The vapor produced can then be incinerated in a gas incinerator.

Catalytic Incineration

Catalytic incineration is also applicable to dilute organic gas streams. In these systems, the gas is preheated by a gas burner and then contacts a catalyst supported in the gas. Oxidation takes place on the surface of the catalyst. Most catalytic reactions can be carried out at lower temperatures, (600 to 1000°F) and result in significant fuel savings. A higher initial investment is required, however (Figure B-7).

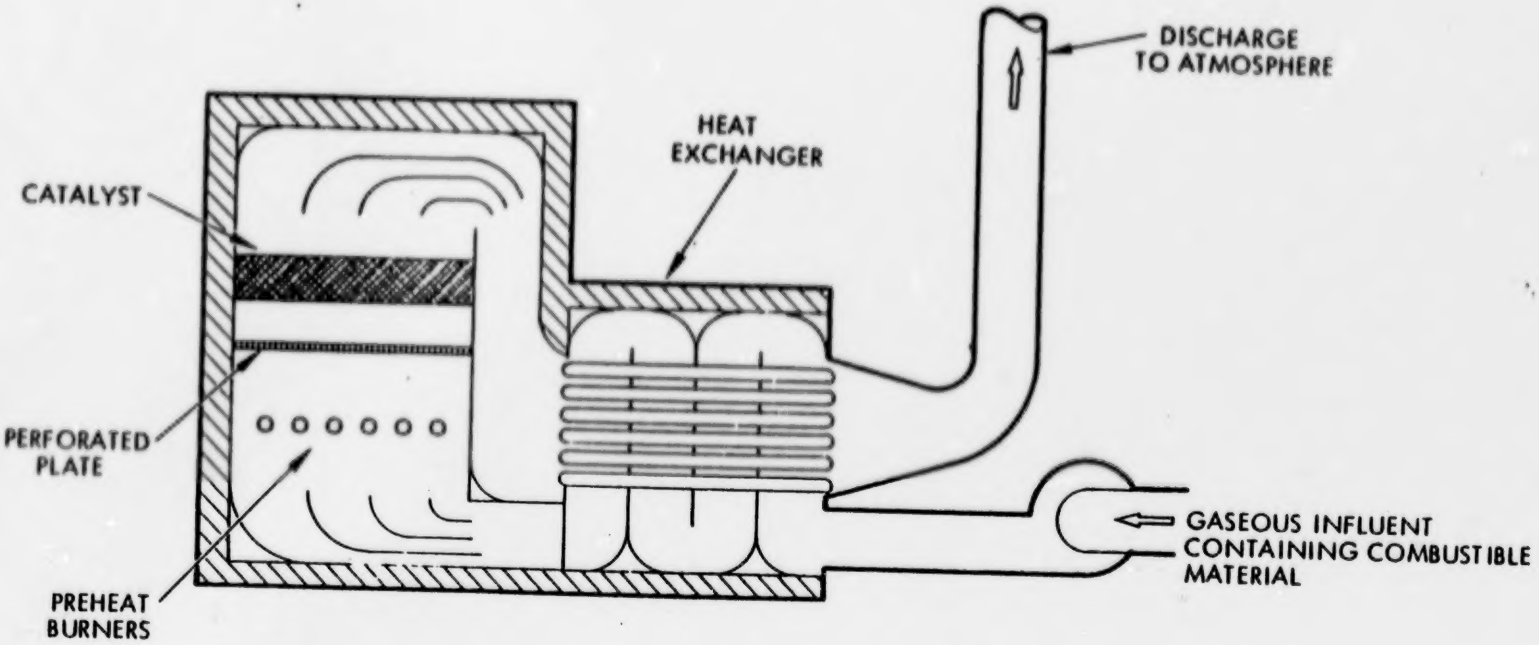

CATALYST
PERFORATED PLATE
PREHEAT BURNERS
HEAT EXCHANGER
DISCHARGE TO ATMOSPHERE
GASEOUS INFLUENT CONTAINING COMBUSTIBLE MATERIAL

Figure B-7. Catalytic incinerator with heat recovery

Since transporting gases over significant distances is not economical, gas incinerators are typically found at the sites of waste gas production. Gas incinerators are common in the chemical process industries for incineration of solvents and the destruction of odorous gases and vapors. Gas incinerators are also used extensively in petroleum refineries for the disposal of waste vapors.

SECONDARY TREATMENT

Wet Collection Equipment

Wet collection equipment can be used to remove both gaseous pollutants and particulate matter. In the collection of gaseous pollutants the primary removal mechanism is the absorption of the gaseous pollutant into a liquid, usually water. For particulate removal, the primary collection mechanism is the impaction of solid particulate material on liquid droplets generated in the scrubber.

Spray Towers/Chambers

A spray tower is a chamber into which water or an aqueous solution is introduced through spray nozzles. The gas stream to be cleaned passes through the chamber. Because of their simple design, spray towers are one of the most economical control devices to purchase and install. They are often used effectively for eliminating gaseous pollution when some of the more soluble pollutants are being treated. Surface contact area, an important consideration in gas absorption, is relatively low compared with that in other types of liquid scrubbers. For this reason, spray towers must be very large to yield efficiencies equivalent to more sophisticated liquid collection systems.

The efficiencies of spray towers for particulate removal are rather low and suitable only for removal of particulate materials ≥10 microns in size. High pressure water has been used to generate a fog spray that will achieve collection efficiencies of the order of 90% for particles in the 1 to 2 micron range.

Packed-Bed Scrubber

A packed-bed scrubber is a tower filled with packing materials, usually plastic, of various shapes that have a high ratio of surface area to volume. These shapes include rings, spiral rings, and berl saddles. Typically, scrubbing liquid passes through this type of system either crosscurrent or countercurrent to gas flow. The interaction of the scrubbing liquid with the packing material produces a high liquid surface area to which the gas stream is exposed.

A condition known as flooding occurs when the upward gas velocity reaches a point at which there is a holdup of the liquid phase on the packing. This situation results in an increased pressure drop across the scrubber and entrainment of liquid by the gas phase. Operation at proper liquid-to-gas flow ratios can achieve high gaseous pollutant removal at relatively low gas flow pressure drops.

The packed-bed scrubber is not often used strictly for particulate removal as gas streams with high concentrations of particulates can plug the bed. Usually, some form of dry collection equipment is used to reduce the particulate load on the packed-bed scrubber.

Wet Cyclone Scrubbers

Wet cyclones are characterized by tangential entry of the gas stream to be cleaned. The gas passes through the cyclone in a helical spiroid path while the liquid is directed outward (centrifugal force) from the center of the circular chamber.

The wet cycline can handle high particulate loadings and produces acceptable collection and removal efficiencies for medium sized (>5 microns) particulate and gaseous pollutants. Where high particulate collection efficiencies are required, a wet cyclone can be used in conjunction with a high efficiency collection unit.

Wet Impingement Scrubbers

This class of wet collection equipment includes self-induced spray scrubbers, orifice plate bubblers, and other scrubbers in which the gas-liquid contact is created by impingement of the gas upon a liquid. This type of equipment is applicable to high particulate loadings; clogging is not a problem as it can be in some wet collectors. Particulate collection efficiency approaches 90% for particles 2 microns and larger. Gas pollutant removal has been reported to be greater than 99%.

Venturi Scrubbers

In venturi scrubbers, the gas passes through a venturi-type constriction, which produces high linear gas velocities. The scrubbing liquid is introduced normal to the gas flow and near the minimum flow area of the venturi. The high gas velocity atmoizes the scrubbing liquid into fine droplets that are maintained in turbulent contact with the gas stream.

Particulate removal in a venturi unit is directly proportional to the gas phase energy input. Gas pressure drops of 10 to 100 in. of water are common with particulate removal approaching 99% at higher pressure drops.(10) Gas pollutant removal efficiencies from 80 to 99% have been reported.

Dry Collection Equipment

Dry collection equipment is used to remove particulate pollutants and to collect powdered solid adsorbents that have been introduced to reduce the stream's gaseous pollutant content. These units have little direct effect on gaseous pollutants. Dry collectors can be used upstream of wet scrubbers to reduce the particulate loading on these units.

Mechanical Collectors

Mechanical collectors remove particulate material by utilizing centrifugal force, gravitational force, or rapid changes in direction of the particulate-laden stream. Types of equipment that fall in this class are settling chambers, baffle chambers, skimming chambers, louver-type collectors, dry cyclones, and impingement collectors. Typical mechanical collectors have particulate collection efficiencies of around 90% for >50 micron-size particles and 50 to 90% efficiencies for 20 to 50 micron-size particles.

Electrostatic Precipitators

Electrostatic precipitators use an electric field for charging the particles in the incoming gas stream. The charged particles then migrate to a collecting electrode. Electrostatic precipitators typically remove 90% of particles 2 microns and smaller.(10) Although electrostatic precipitators require a larger initial investment than comparable wet collectors, operating costs are significantly less. Wet electrostatic collectors have been introduced.

Fabric Filters (Bag Houses)

Fabric filters collect particulate material as the gas stream passes through a fabric bag. A filter-like cake builds up on the fabric and the pressure drop through the bag increases. When the cake has built up to the optimum thickness it is either shaken loose or blown off and falls into a collection hopper. Particle collection efficiency for these units often exceeds 99%. Fabric filters cannot be used with wet gas streams or at high temperatures (>600°F).(10)

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